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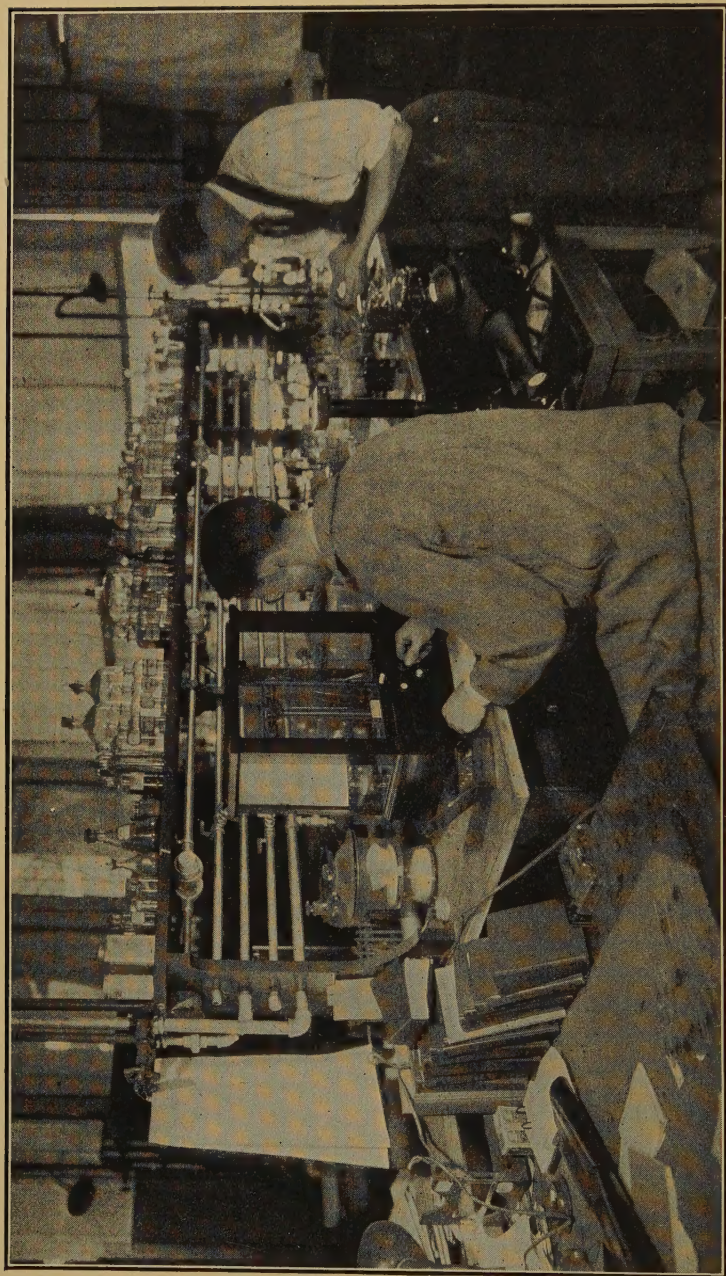
ESSENTIALS OF  
QUALITATIVE CHEMICAL  
ANALYSIS











"Back of the great manufacturing enterprises is the painstaking procedure of the analytical laboratory."—The Bakelite Corporation, New York City.

*Frontispiece*

# ESSENTIALS OF QUALITATIVE CHEMICAL ANALYSIS

WITH

A SPECIAL DEVELOPMENT OF THE FUNDAMENTAL  
THEORETICAL PRINCIPLES AND THEIR APPLICA-  
TIONS IN MODERN ANALYTICAL PROCEDURE

BY

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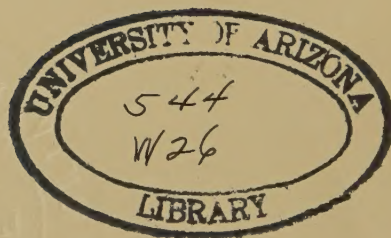
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## PREFACE

*(Written Primarily for the Student)*

THE importance of analytical determinations cannot be overestimated. They supply the fundamental data upon which industrial operations may be successfully carried out. The composition of many substances determines their value and a trace of an undesirable ingredient often renders the entire product worthless.

To be present in the laboratory of a large industrial plant while determinations are being made of a product, as it goes through one process after another on its way to completion, will help one to realize with what a vital problem the analyst is dealing. There are no dull moments in the analytical laboratory, and, instead of the work lapsing into a monotonous routine, there are constantly developing new combinations of reactions, the intelligent handling of which requires the highest skill that can be given.

With qualitative analysis you are taking one of the first steps that may lead to the career of a successful analyst. Your attitude will determine very largely whether you succeed or not. Your familiarity with the units with which you are ultimately going to accomplish things must be thorough. These units are called ions. The laws which express how ions react are not especially difficult, but they must be studied from many angles until you can almost visualize them instead of falling back upon an algebraic equation. The old saying, "It's only the hits that count," never had a better application than in analytical work. But what can arouse greater enthusiasm than the game that requires reasonable skill? The indifferent pounding of a ball around a lot is not especially interesting and may finally become tiresome, but the game of skill! That's another matter.

This book is written in the hope that it may help you to play the ion game in such a way that success is almost certain to follow.

Part I reviews some of the material introduced in general chemistry and then develops the underlying principles that govern the reactions in which ions take part. Formulas are derived, problems

to illustrate the various methods of approach are worked out in full and everything is presented that can in any way assist in the thorough mastering of the various relationships. Each topic is summarized, and with a set of exercises the principles are applied, not reviewed as is generally done. It is by this final application that the truth is brought home.

Part II consists of preliminary tests in which are developed the specific ionic reactions of the cations that are finally incorporated into a scheme of analysis. You are constructing the method of procedure that you will eventually use and by so doing are enabled to handle intelligently what you helped to assemble. You are not merely following a road map where you are directed to turn right or turn left but you are actually going over a continuous journey which you have traveled sectionally before. Many questions are introduced during the preliminary work that involve the application of the theoretical principles which were presented in a previous section to the actual ionic reactions being performed. You never lose sight of the fact that qualitative analysis is not necessarily an end in itself but a most efficient means of developing chemical reasoning power which may prove invaluable in later research work. Your final goal is surely not to be a weigher of samples in a large routine laboratory. You are supplied with a set of notes in the systematic scheme of analysis which follows the preliminary tests. These notes should be of very great assistance in the analysis of practice unknown solutions. They present you with suggestions and words of caution in analytical procedure which have been obtained by the supervision of several hundred students. You are profiting by the experience of many.

Part III deals with the anions in the manner outlined for the cations, and Part IV combines the procedures for the complete analysis of a sample. Where the sample is a solid consisting of mixed powders, an alloy or a technical product, the method most suitable for putting it into solution is given.

Part V contains several tables and lists of supplies and solutions that will prove of great assistance in the setting up and maintenance of a qualitative laboratory.

Throughout the text there has been a liberal use of diagrams and photographs. This material not only presents certain features better than the printed page but does so in a most interesting manner. The value of visual methods of education is so well estab-



lished that no defense need be given here. Some may say that the entire laboratory work is visual, why add more? And so is a trip to a foreign country; but how valuable are pictures and charts even there! You are enabled to gain information concerning places that it may be impossible to visit, and the pictures also make permanent records for more careful study in the future of casual impressions that would otherwise be indistinct and often inaccurate. Qualitative analysis should be just as interesting as general chemistry or industrial chemistry and we hope that this text will help make it so.

Of special interest are the plates in color. You may be an expert in color, but to interpret the many time-worn expressions customarily used in an attempt to assist the student in visualizing a forthcoming flame test, colored solution or colored precipitate would require an intimate knowledge of the birds of the air, the flowers of the field and various building materials, as well as a sense of humor. An examination of the following list will make the point clear: canary yellow, lilac, lavender, straw-color, brick red, reddish-brown, brownish-red, orange, carmine; and the gem, especially if you are in a cosmopolitan class, is "flesh color." One author states that the color of a calcium flame is "red." Look up red in a color chart, mark it and then make the flame test. Decide for yourself how much assistance you received. It is very difficult to form a mental picture of a color with which you have not been associated, especially one of the type of lilac or straw-color. Many times tests are ruined even in the preliminary work because the color obtained did not correspond to that expected by the student. The perchromic acid test for a chromate gives a blue solution in ether. Frequently in the preliminary tests a satisfactory result is not obtained, and later in an unknown, a greenish solution results which may be mistaken for the chromate test. By having color plates for comparison this common source of error should be eliminated. The color work is either from color photographs or photographs tinted in color and the colors are matched by means of a colorimeter.

The text is arranged so that when there is not sufficient time to go through the preliminary reactions the student can follow the schemes of analysis and refer to the preliminary sections as desired. The reactions and equations are sufficiently complete to make reference to a more detailed book seldom necessary.

In keeping with the modern development of the subject, the quantitative phase has been introduced as far as possible. Test solutions contain definite quantities of radicals and the procedure instructions specify the number of cubic centimeters and the concentrations of reagents to be used. By comparison with the amount of precipitate that was formed during the preliminary tests, a good approximation can be made of the amount of radical present in the solution which is being analyzed.

At the end of each procedure for the systematic analysis, there are included many optional tests. This enables additional confirmatory tests to be made, as well as modifications of the procedure to suit local conditions or preferences.

All valence exponents greater than two are represented by plus and negative exponents rather than a group of plus or minus signs crowded with greater or less efficiency (and legibility) after the radical.

The author wishes to express his thanks to Dr. Leo Lehrman and Dorothy M. Ware of the Chemistry Department of Washington Square College, New York University. Dr. Lehrman has read the entire manuscript and has been of great assistance in checking the mass of details that must be incorporated in a text on analytical chemistry. The author's daughter has assisted in the manuscript revisions and in reading proof.

Acknowledgment is due the following for supplying photographs, the majority of which were specially taken for this publication: Bakelite Corporation, New York City; Bausch & Lomb Optical Company, Rochester, N. Y.; Bureau of Standards, Washington; Commercial Solvents Corporation, Terre Haute, Ind.; Die Badische Anilin & Soda-Fabrik, Germany; Eastman Kodak Company, Rochester, N. Y.; Eimer & Amend, New York City; Franz Schmidt & Haensch, Berlin; La Motte Chemical Products Company, Baltimore, Md.; Norton Company, Worcester, Mass.

During the preparation of this text constant reference has been made to the standard texts and reference books on the subject. Credit is here given for whatever assistance has been obtained from this source.

J. C. WARE

June, 1928.

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# ESSENTIALS OF QUALITATIVE CHEMICAL ANALYSIS

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## PART I FUNDAMENTAL PRINCIPLES

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### CHAPTER I INTRODUCTION

If we are given a substance to analyze, our problem is to find out what is in it. If it is merely a question of what units are present, the problem involves qualitative analysis. On the other hand, if the amounts are desired, further determinations must be carried out, and that is the purpose of quantitative analysis. Of necessity, the qualitative tests precede the quantitative.

The special field where the majority of reactions in analysis are performed is the solution, and it will therefore be necessary to review some of the facts concerning solutions and become reasonably familiar with the laws and principles which govern reactions in solution. Systematic analysis, when performed intelligently, not only leads to accurate results but is also done with that degree of pleasure and satisfaction which accompanies any of our activities when we know what we are doing, and the underlying reasons for doing it.

#### THE SOLUTION

A small amount of common salt when added to water will be taken up by the water and become invisible. We say that it has gone into solution. The salt is the **solute** and the water, the **sol-**

**vent.** If we were to consider all of the things that have taken place during solution we should find it a very complicated matter, but for our purposes it will suffice to know that a **solution** is homogeneous, that is, of uniform composition throughout and that it remains so, which, of course, precludes any of the salt settling out (compare with colloidal suspensions on page 83). The salt solution is also capable of conducting an electric current and is therefore an **electrolyte**. Acids, bases and salts have this property. A sugar solution will not act as an electrolytic conductor and is a **non-electrolyte**. In analytical work, solids, liquids or gases may be the substances in solution while liquids are the only common solvents. It is possible, however, to have solutions consisting of other combinations than the ones just given.

It is unfortunate that we do not have two different expressions to represent the two different types of solution as illustrated by the solution of salt in water and the solution of zinc in hydrochloric acid. The first involves the physical solution of salt in water and the second requires a chemical reaction between the zinc and the hydrochloric acid with a subsequent physical solution of the zinc chloride.

The **limit of solution** is a very definite thing and depends upon the nature of the solute and solvent and the temperature, and with gases upon the pressure also. All of this means that if we are dissolving salt in water at  $20^{\circ}$ , a certain definite weight will always go into solution in a definite weight or volume of water, and if another solvent is used, another weight will go into solution. A **saturated solution** is one that is in equilibrium when placed in contact with an excess of solute, and the constant values are given in **solubility tables** or represented in **solubility curves**. A solution that is still capable of dissolving more of the solute is **unsaturated** and its concentration is expressed in terms of units representing saturated solutions. A **supersaturated** solution is in an unstable equilibrium and, where the conditions are favorable, will precipitate out the excess of solute over that required for stable equilibrium. The actual amount of solute is in excess of that required for a normally saturated solution but the excess is prevented from coming out by inability to form the solid. Dust particles, crystals or even scratches on the inside of the container will start precipitation.

**Dilute and concentrated** solutions refer to the actual amount of solute present and not to the degree of saturation. The terms



are purely relative, and what one person might consider dilute might appeal to another as very concentrated.

Solubilities can be expressed in **physical units**, as grams of solute per 100 grams of solvent, or grams of solute per 100 grams of solution. The term per cent saturation or degree saturated involves the saturated concentration as the unit of measurement. The chemist is more interested in the concentration in molecules, or atoms or ions, and so he uses **chemical units** that will give him this information. A **molar** solution contains a mole of solute per liter of solution. A **mole** is a gram-molecular weight, and a **gram-molecular weight** is the certain number of grams which is numerically equal to the molecular or **formula weight** of the substance. To make up a molar solution of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , we must take the entire formula weight in grams, 286.15 grams, place in a liter flask and add water until we have a liter of solution. A **gram-atomic weight** is the number of grams that is the same numerically as the atomic weight, and the **gram-ion** is the result of a gram-atomic weight ionizing. There are no corresponding chemical terms for concentrations involving these last two weights.

Another important chemical concentration unit is a **normal solution**. Such a solution contains one gram of reacting hydrogen or its **reacting equivalent** per liter of solution. For example, 36.46 grams of  $\text{HCl}$  contain one gram of replaceable hydrogen, and this weight, made up to a liter of solution, is normal. One-half a formula weight of  $\text{H}_2\text{SO}_4$  will be required in making a normal solution, or the formula weight in this case could be made up to 2 liters for a normal solution. With  $\text{AlCl}_3$ , since the valence of Al is +3, a formula weight of the salt will contain three reacting equivalents of the metal. A normal solution must always contain one reacting equivalent of the metallic portion per liter of solution. Molar and normal concentrations are abbreviated in terms of decimals of  $m$  and  $n$ .

An increase in temperature usually increases the solubility of a substance. Sometimes the increase is gradual, and at other times a small increase in temperature will enormously increase the solubility. The solubility of  $\text{NaCl}$  is very slightly increased from  $0^\circ$  to  $100^\circ$  while the solubility of  $\text{Ca}(\text{OH})_2$  is actually decreased.

The solubility of a gas is very greatly decreased with a rise in temperature and a decrease in pressure. Boiling is therefore used to drive out gases from liquids.

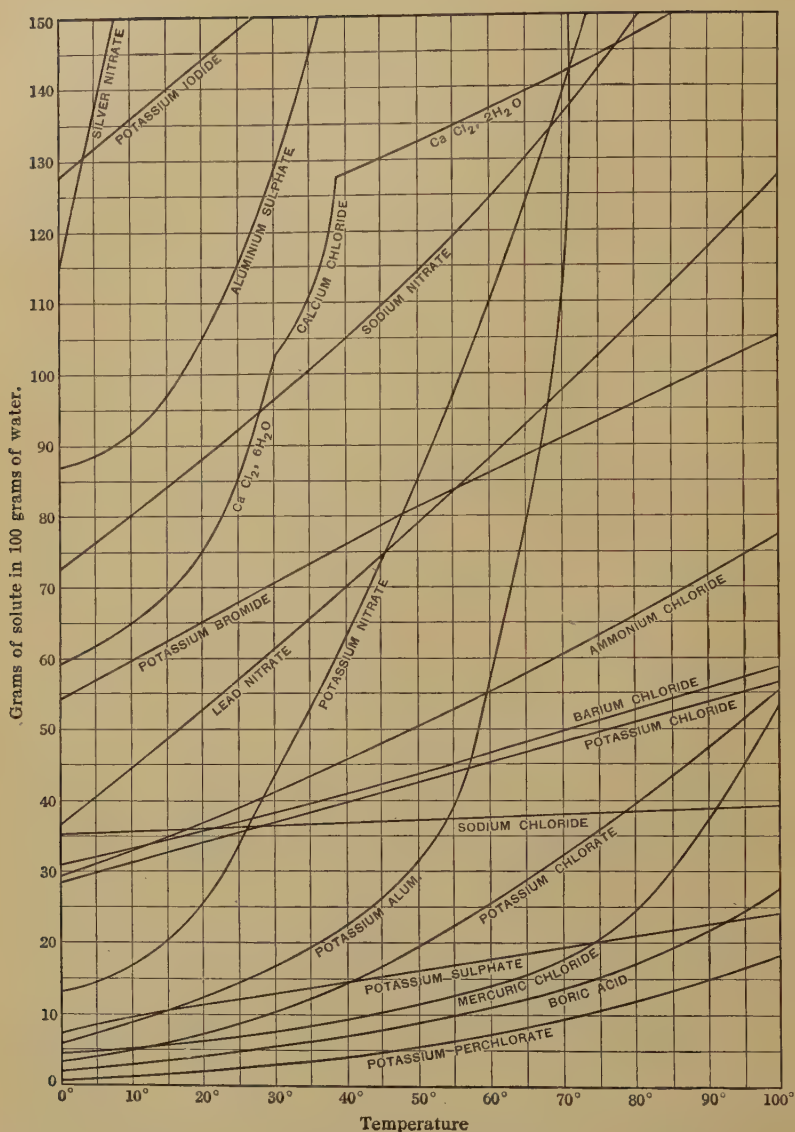


FIG. 1.\*—Influence of Temperature on the Solubility of Certain Salts in Water.

\* Taken from Smith's "Inorganic Chemistry," by Kendall. The Century Co., 1927.

Certain liquids and all gases are completely miscible, and solutions may therefore be obtained of any proportion. Alcohol and water are examples of miscible liquids. Very often an increase in temperature may increase miscibility; and it may also accomplish the reverse.

We shall next consider the important properties of solutions as embodied in ionization, and the fundamental laws concerning the reactions of ions.

TABLE I \*  
SOLUBILITIES OF BASES AND SALTS IN WATER AT 18°

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95 3.9	35.86 5.42	77.79 13.3	0.0313 0.059	0.3 0.013	37.24 1.7	51.09 3.0	73.19 5.4	55.81 5.1	203.9 9.2	1.49 0.05
Br	65.86 4.6	82.76 6.9	168.7 12.6	0.041 0.066	0.042 0.0215	103.6 2.9	96.52 3.4	143.3 5.2	103.1 4.6	478.2 9.8	0.598 0.02
I	137.5 6.0	177.9 8.1	161.5 8.5	0.0635 0.071	0.006 0.0317	201.4 3.8	169.2 3.9	200.0 4.8	148.2 4.1	419.0 6.9	0.08 0.022
F	92.56 12.4	4.44 1.06	0.27 0.11	195.4 13.5	72.05 3.0	0.16 0.0292	0.012 0.001	0.0016 0.032	0.0087 0.0214	0.005 0.035	0.06 0.002
NO <sub>3</sub>	30.34 2.6	83.97 7.4	71.43 7.3	213.4 8.4	8.91 0.35	8.74 0.33	66.27 2.7	121.8 5.2	74.31 4.0	117.8 4.7	51.66 1.4
ClO <sub>3</sub>	6.6 0.52	97.16 6.4	313.4 15.3	12.25 0.6	8.69 0.13	35.42 1.1	174.9 4.6	179.3 5.3	126.4 4.7	183.9 5.3	150.6 3.16
BrO <sub>3</sub>	6.38 0.38	36.67 2.2	152.5 8.20	0.59 0.025	0.30 0.009	0.8 0.02	30.0 0.9	85.17 2.3	42.86 1.5	58.43 1.8	1.3 0.03
IO <sub>3</sub>	7.62 0.35	8.33 0.4	80.43 3.84	0.004 0.0314	0.059 0.0216	0.05 0.001	0.25 0.0257	0.25 0.007	6.87 0.26	0.83 0.02	0.002 0.043
OH	142.9 18.0	116.4 21.0	12.04 5.0	0.01 0.001	40.04 1.76	3.7 0.22	0.77 0.063	0.17 0.02	0.001 0.032	0.035 0.045	0.01 0.034
SO <sub>4</sub>	11.11 0.62	16.83 1.15	35.64 2.8	0.55 0.020	4.74 0.09	0.023 0.0410	0.011 0.036	0.20 0.015	35.43 2.8	53.12 3.1	0.0041 0.0313
CrO <sub>4</sub>	63.1 2.7	61.21 3.30	111.6 6.5	0.0025 0.0315	0.006 0.031	0.0335 0.0414	0.12 0.006	0.4 0.03	73.0 4.3	...	0.042 0.065
C <sub>2</sub> O <sub>4</sub>	30.27 1.6	3.34 0.24	7.22 0.69	0.0034 0.0317	1.48 0.030	0.0085 0.0338	0.0046 0.026	0.0355 0.0443	0.03 0.0027	0.0364 0.044	0.0316 0.0554
CO <sub>3</sub>	108.0 5.9	19.39 1.8	1.3 0.17	0.003 0.031	4.95 0.10	0.0023 0.0311	0.0011 0.047	0.0013 0.0313	0.1 0.01	0.0047 0.0337	0.031 0.043

The upper number in each square gives the number of grams of the anhydrous salt held in solution by 100 c.c. of water. The lower number is the molar solubility, i.e., the number of moles contained in one liter of the saturated solution. The numbers for small solubilities have been abbreviated. Thus 0.064 = 0.0000064

\* Taken from Smith's "Inorganic Chemistry," by Kendall. The Century Co., 1927.

To find grams of salt in 100 c.c. saturated solution  
multiply molecular wt. by molar solubility and  
divide by 10. or molar wt. x molar solubility

✓ **Summary.**—Analysis determines the composition of a substance. Qualitative analysis has to do with the kind of units present, and quantitative, with the amounts.

A true solution consists of a solute subdivided in a solvent in such a manner that the result is homogeneous and non-settling, and the particles do not exceed molecular magnitudes.

Solutions of acids, bases and salts are classified as electrolytes, and conduct the electric current.

Solutions are classified as unsaturated, saturated and super-saturated with reference to the maximum amount of solute that can be held by the solvent in stable equilibrium. Dilute and concentrated solutions refer to the relatively small or large amounts of solute present and have nothing to do with the degree of saturation.

Concentrations are expressed in physical units as, for instance, grams of solute per 100 grams of solvent or 100 grams of solution. Per cent saturation and degree of saturation are also used. Molarity and normality are chemical units. A molar solution contains a gram-formula weight per liter of solution and a normal solution contains a reacting equivalent of the metallic radical per liter of solution. Equivalent solutions contain equivalent reacting weights of the metallic portion.

An increase in temperature usually increases the solubility of a solid but decreases the solubility of a gas.

Miscible liquids are mutually soluble in all proportions.

### EXERCISES

1. By referring to the solubility curves, determine the approximate solubility of:

Barium chloride at 85°;

Potassium bromide at 30°; 71

Sodium chloride at 90°. 39

2. What is the increase in solubility of potassium alum from 50° to 60° 32-57

3. Eight hundred cubic centimeters of a solution saturated with potassium perchlorate at 90° are cooled to 35°. What weight of solid will crystallize out?

4. Given a solution of 0.2n  $\text{Na}_2\text{CO}_3$ , what would be the equivalent molar concentration of  $\text{HCl}$ ? Of  $\text{H}_2\text{SO}_4$ ? 0.2M 0.1M

5. What is the meaning of a curve (a) that is straight? (b) That bends upward at a low temperature? (c) That bends upward at a much higher temperature?

6. What is a gram-molecular weight of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ? Of  $\text{Al}(\text{OH})_3$ ? 199.4 78

7. Can a molar solution of each be made up?

$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  yes



8. What weight of  $\text{HNO}_3$  is in 500 cc. of a normal solution? What is its molarity? *1m*

9. What weight of  $\text{H}_2\text{SO}_4$  is in 1 cc. of 0.1n  $\text{H}_2\text{SO}_4$ ? What is its molarity? *0.05m*

10. If 1.5 cc. of 0.1n  $\text{HCl}$  are required to neutralize 15 cc. of  $\text{Ca}(\text{OH})_2$  solution, what is the normality of the base? *.005n*

11. A reagent bottle on your desk is marked 13m. How would you make up 2 liters of a 0.1n solution? *2000 / 130 = 15.38 cc in 1 l. of HCl*

12. You have a solution that is 0.34m. How much 0.1n can be made from it, and how would it be done? You are to supply any further data necessary.

*take*

*3.4 times as much. 1 l. can be made*

*If 1 l. of .34m add enough water  
to make 3.4 liters of .1n.*

## CHAPTER II

### IONS AND IONIZATION

Reactions in qualitative analysis occur very largely in solutions, and in making a solution a certain type of **dissociation**, generally known as **ionization**, takes place. For example, if some NaCl is dissolved in water it is believed that the molecules of the salt are broken down more or less completely, by the solvent, into smaller bodies known as **ions**. The essential differences between these subdivisions and the original unit is that the ions are **electrically charged**, and very highly so when their smallness is considered, and their properties are radically different. The differences between NaCl and its ions are as great as between three entirely different elements.

The theory of ionization was first specifically presented by Arrhenius,<sup>1</sup> and the main assumptions are the following: (a) When an electrolyte<sup>2</sup> or ionogen is dissolved it is more or less completely dissociated into smaller particles known as ions.<sup>3</sup> (b) The ions are resolved into two groups, one carrying positive electrical charges and the other negative charges. The charged particles, or ions, are frequently referred to as **radicals** and may consist of a single atom, as  $\text{Na}^+$  and  $\text{Cl}^-$ , or a group of atoms, as  $\text{NH}_4^+$  and  $\text{SO}_4^-$ .<sup>4</sup> (c) The number of positive ions is not necessarily equal to the number of negative ions, but the sum of the positive and negative charges on all ions from one molecule will algebraically equal zero. That is, the molecule is essentially neutral. This is known as the **law of electrical equivalence**.

Ions from the same molecule do not necessarily carry the same

<sup>1</sup> Zeitschr. physikal. Chem., **1**, 631 (1887).

<sup>2</sup> A substance that in solution conducts the electric current.

<sup>3</sup> Care must be exercised in consulting articles on ionization, especially the earlier ones, because these final subdivisions in solution were often referred to as molecules. Unfortunately, this term is still carelessly used in certain recent publications.

<sup>4</sup> Walker and a few others represent the positive and negative ions in this manner:  $\text{Na}^+$ ,  $\text{Cl}'$ .

number of charges. The following examples will show some of the possibilities:  $\text{NaCl}$  ionizes into  $\text{Na}^+$  and  $\text{Cl}^-$ ,  $\text{Na}_2\text{SO}_4$  ionizes into  $2\text{Na}^+$  and  $\text{SO}_4^{--}$ ,  $\text{AlCl}_3$  ionizes into  $\text{Al}^{+3}$  and  $3\text{Cl}^-$ .

An ion carrying one charge, either positive or negative, is **univalent**; with two charges it is **bivalent**, and with three charges it is **trivalent**, etc. Salts are often grouped with reference to the valences of their radicals, as:  $\text{NaCl}$  is of the uni-univalent type,  $\text{Na}_2\text{SO}_4$  or  $\text{BaCl}_2$  is uni-bivalent, and  $\text{CaSO}_4$  bi-bivalent.

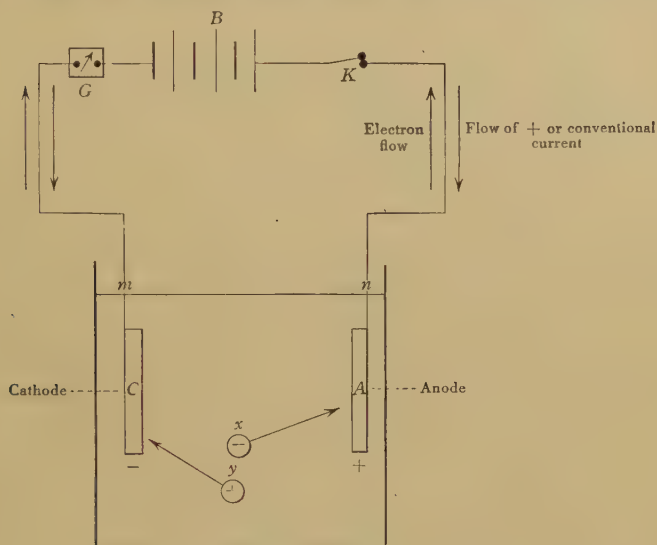


FIG. 2.—Direction of Flow of Ions in an Electrolytic Cell.

*B*, battery; *G*, galvanometer; *K*, switch; *A* and *C*, electrodes; external circuit from *m* to *n* by way of *B*, etc.; *x*, negatively charged ion moving towards the anode and is therefore an anion; *y*, positively charged ion moving towards the cathode and is therefore a cation.

In the **conductance** of an electric current by a solution it is believed that the ions do approximately all of the **transference**. The electric current does not cause ionization. The ions are present before the current is turned on. The current, however, separates the ions, and the charge on the ion is inferred by noting the electrode at which it is discharged. The ions are named according to the electrode to which they travel and not according to the charge which they carry. A negatively charged ion travels to the plus electrode, which is known as the **anode**, and the ion is an **anion**. The plus ion, going to the negative electrode, or **cath-**

ode, is the **cation**. Metals yield plus ions, hence metallic analysis is known also as the analysis for cations.

It has been established that the ions move or **migrate** independently in a solution and at different rates. The motion, however, is comparatively slow as shown in the following table:<sup>5</sup>

TABLE II  
ABSOLUTE IONIC VELOCITIES

+ Ion	Velocity in Cm. per Sec.	- Ion	Velocity in Cm. per Sec.
H <sup>+</sup>	0.00320	OH <sup>-</sup>	0.00181
K <sup>+</sup>	0.00066	Cl <sup>-</sup>	0.00069
Ag <sup>+</sup>	0.00057	NO <sub>3</sub> <sup>-</sup>	0.00064
NH <sub>4</sub> <sup>+</sup>	0.00066	Cr <sub>2</sub> O <sub>7</sub> <sup>=</sup>	0.00047

It is worth noting that H<sup>+</sup> and OH<sup>-</sup> are in a class by themselves as far as speed is concerned, with H<sup>+</sup> far in the lead. The rest of the anions and cations do not present great differences in velocities. The number of charges does not seem to affect the speed greatly.

**The color of a solution** may be due to that of the dissolved molecules, or of one of the ions, or of both. For example, anhydrous CuBr<sub>2</sub> is black, and a concentrated solution of this salt in which there is little ionization is brown. If the solution is diluted with water it will be noted that, as ionization increases, the color changes with the formation of the greenish-blue Cu<sup>++</sup> ion, and finally, when the solution is so dilute that most of the molecules are ionized, the color will be the characteristic blue of the Cu<sup>++</sup> ion alone. (See Plate I, G and H.) A solution of Fe(SCN)<sub>3</sub> is a shade of red (see Plate I, A), and we know the color is due to the dissolved molecule, because in other compounds containing Fe<sup>+3</sup> and SCN<sup>-</sup> there is never the same red color developed. The color characteristics of ions are given at the beginning of each analytical group and should be very carefully noted.

**The degree of ionization** is quite sensitive to changes in concentration. Dilution promotes ionization by increasing the solvent which is necessary for ionization. Although the variation of per cent ionization with concentration is an inverse one, it must

<sup>5</sup> Getman's "Outlines of Theoretical Chemistry." Data have been rearranged.



not be inferred that it involves the first powers of ionization and concentration. For example, the per cent ionization is increased by making the concentration one-half its former value, but it is not doubled. A numerical problem in which the effect of dilution can be noted is given in the section on the ionization constant,<sup>6</sup> page 35.

All electrolytes are supposed to be completely ionized at infinite dilution; but by reference to the following table it can be seen that, in 0.001*m* solutions, strong acids and bases are ionized nearly 100 } per cent.

TABLE III \*  
PERCENTAGE DISSOCIATION OF ACIDS AND BASES AT 18°

Electrolyte	Concentration in Gram-equivalents per Liter						
	0.001	0.002	0.005	0.01	0.02	0.05	0.1
HCl	99.0	98.6	98.1	97.2	95.7	94.4	92.0
HNO <sub>3</sub>	99.0	98.6	.....	96.9	.....	93.8	92.0
CH <sub>3</sub> CO <sub>2</sub> H	11.7	8.6	5.7	4.17	3.0	1.8	1.34
NaOH (25°)	97.1	95.5	94.8	93.3	.....	.....	90.5
NH <sub>4</sub> OH	11.7	8.6	5.5	4.07	3.0	1.9	1.31

\* Taken from Creighton and Fink's "Electrochemistry," John Wiley & Sons, Inc., New York, 1928, vol. I, p. 105.

Since we are to deal very largely with ions in our reactions it is necessary to remember that the solutions must be diluted to such a degree that the substance is largely ionized. Many times a reaction is unsatisfactory because the solution is too concentrated, or the high concentration may have developed a type of reaction entirely different from the one desired.

A very common error is to relate incorrectly the per cent ionization with the total number of ions present per unit volume of solution. It does not follow that a sum of money placed at a certain rate of interest will yield a larger return than a larger sum at a lower rate of interest. The amount of money at interest is a factor that must be considered, as well as the rate of interest.

<sup>6</sup> For a more mathematical treatment of the effect of dilution upon per cent ionization, consult Ostwald's dilution law and the various formulas that have been developed from it. Any physical chemistry contains the material.

So in ionization, if we use a more dilute solution of an acid, for example, the per cent ionization is increased, and, since the total number of dissolved molecules in the total volume of solution is the same, it follows that the total number of ions in the solution is correspondingly increased. The acidity, however, is not increased by dilution because it is based upon the number of  $H^+$  ions in unit volume and not in the total volume. If to one volume of the acid nine volumes of water have been added, the concentration of acid molecules is one-tenth. Now, if the per cent ionization were the same, the ion concentration per unit volume would be one-tenth of its former value. The ion concentration per unit volume, however, due to increase in per cent ionization, has not been quite decreased to one-tenth, but the  $H^+$ -ion concentration per unit volume has certainly not been increased even though there has been an increase in the total number of ions in the entire volume. (The total number of ions present and the ion concentration per unit volume must be clearly distinguished in dilution problems.

The ionization of polybasic acids must be especially noted. Sulfuric acid, for example, evidently ionizes in stages; it first yields  $H^+$  and  $HSO_4^-$ , and the latter then breaks up into  $H^+$  and  $SO_4^{2-}$ . When sulfuric acid reacts with sodium chloride, the acid salt  $NaHSO_4$  is first formed, and finally the product is  $Na_2SO_4$ . By adjusting the proportions of the reacting substances it is possible to obtain the acid salt almost entirely. The first  $H^+$  that is ionized is due to **primary ionization**; the second  $H^+$  constitutes **secondary ionization**; and if the acid had a third available acid hydrogen, as with  $H_3PO_4$ , a **tertiary ionization** would be possible.

The ionizations just referred to do not take place to the same degree. The primary is always much greater than the secondary; and the tertiary, if it takes place at all, is usually very insignificant. The three values for phosphoric acid, when expressed in per cent, are as follows: primary, 27; secondary, 0.0000002; tertiary, 0.00000000000034.

Where the degree of ionization is given in tables, it must be definitely known for what concentration it is computed. Sometimes the ionic concentration includes all types of ionization.<sup>7</sup>

<sup>7</sup> With phosphoric acid the primary ionization is the only one of consequence; but with sulfuric acid, where the primary is 38 per cent and the secondary is 20 per cent, it makes a big difference whether the  $[H^+]$  from all sources or from the primary or secondary ionization is designated.

Since tables showing the degree of ionization of various substances are meaningless unless the concentration is given, 0.1*n* solutions are usually inferred if no value is specifically stated.

TABLE IV

DEGREE OF IONIZATION, EXPRESSED IN PER CENT, OF SOME COMMON ACIDS, BASES AND SALTS IN 0.1*n* CONCENTRATION AT 18°

	Ions Formed	Per Cent
Acids: HNO <sub>3</sub>	H <sup>+</sup> , NO <sub>3</sub> <sup>-</sup>	92.00
HCl	H <sup>+</sup> , Cl <sup>-</sup>	92.00
H <sub>2</sub> SO <sub>4</sub>	2H <sup>+</sup> , SO <sub>4</sub> <sup>-</sup>	61.00
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	H <sup>+</sup> , HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	50.00
H <sub>3</sub> PO <sub>4</sub>	H <sup>+</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	27.00
H <sub>2</sub> F <sub>2</sub>	2H <sup>+</sup> , 2F <sup>-</sup>	15.00
CH <sub>3</sub> COOH	H <sup>+</sup> , CH <sub>3</sub> COO <sup>-</sup>	1.34
H <sub>2</sub> CO <sub>3</sub>	H <sup>+</sup> , HCO <sub>3</sub> <sup>-</sup>	0.17
H <sub>2</sub> S	H <sup>+</sup> , HS <sup>-</sup>	0.07
H <sub>3</sub> BO <sub>3</sub>	H <sup>+</sup> , H <sub>2</sub> BO <sub>3</sub> <sup>-</sup>	0.01
HCN	H <sup>+</sup> , CN <sup>-</sup>	0.01
Bases: KOH	K <sup>+</sup> , OH <sup>-</sup>	91.00
NaOH	Na <sup>+</sup> , OH <sup>-</sup>	91.00
Ba(OH) <sub>2</sub>	Ba <sup>+</sup> , 2OH <sup>-</sup>	77.00
NH <sub>4</sub> OH	NH <sub>4</sub> <sup>+</sup> , OH <sup>-</sup>	1.34
Salts: KCl	K <sup>+</sup> , Cl <sup>-</sup>	86.00
KNO <sub>3</sub>	K <sup>+</sup> , NO <sub>3</sub> <sup>-</sup>	83.00
CH <sub>3</sub> COOK	K <sup>+</sup> , CH <sub>3</sub> COO <sup>-</sup>	83.00
K <sub>2</sub> SO <sub>4</sub>	2K <sup>+</sup> , SO <sub>4</sub> <sup>-</sup>	72.00
K <sub>2</sub> CO <sub>3</sub>	2K <sup>+</sup> , CO <sub>3</sub> <sup>-</sup>	71.00
NH <sub>4</sub> Cl	NH <sub>4</sub> <sup>+</sup> , Cl <sup>-</sup>	85.00
NaHCO <sub>3</sub>	Na <sup>+</sup> , HCO <sub>3</sub> <sup>-</sup>	78.00
ZnSO <sub>4</sub>	Zn <sup>++</sup> , SO <sub>4</sub> <sup>-</sup>	40.00
HgCl <sub>2</sub>	Hg <sup>++</sup> , 2Cl <sup>-</sup>	1.00
Hg(CN) <sub>2</sub>	Hg <sup>++</sup> , 2CN <sup>-</sup>	trace only
Water: H <sub>2</sub> O	H <sup>+</sup> , OH <sup>-</sup>	0.000000142

The degree of ionization of water is referred to the per cent ionized in a liter and not in a 0.1*n* solution, for the reason that H<sub>2</sub>O would then be the solvent as well as the solute. The actual calculation is as follows:

$$\frac{1000 \text{ grams water in one liter}}{18 \text{ grams}} = 55.5 \text{ moles of water per liter.}$$

The concentration of  $H^+$  at  $18^\circ$ , in terms of normality, is  $0.789 \times 10^{-7}$ , which is the average of the results obtained by Kohlrausch and Heydweiller =  $0.768 \times 10^{-7}$ ; Lorenz and Böhi =  $0.848 \times 10^{-7}$ ; Michaelis =  $0.860 \times 10^{-7}$ ; and Noyes =  $0.678 \times 10^{-7}$ .

Then,

$$\begin{aligned} \text{Per cent ionized} &= \frac{0.789 \times 10^{-7}}{55.5} \times 100 \\ &= 0.000000142 \end{aligned}$$

By making a study of the ionization data it can be seen that acids readily group themselves into four classes: (a) strong, as nitric acid, the halogen acids, ( $H_2F_2$  excepted), and sulfuric acid; (b) intermediate, as phosphoric acid and hydrofluoric acid; (c) weak, as acetic acid and carbonic acid; (d) extremely weak, as hydrosulfuric acid, boric acid, and hydrocyanic acid. It might be well to notice the position of oxalic acid, which, as the table will show, is a much stronger acid than is usually supposed, perhaps by a comparison with the organic acid, acetic acid, which is very weak.

The bases also show a very wide range in ionization, and arbitrary divisions can also be made with them as with acids. The value for  $Ca(OH)_2$  is not given because a saturated solution at room temperature is only about  $0.02m$ , hence a  $0.1n$  solution is impossible. When it is known that a  $n/64$  solution is ionized about 90 per cent, the strength of calcium hydroxide as a base can be indirectly calculated in terms of a  $0.1n$  solution, or solutions of  $n/64$  strength of other bases can be determined for a direct comparison. In this way it is found that calcium hydroxide, as one would suppose, has a strength about equal to the hydroxides of barium and strontium.

Salts as a group are highly ionized. The **uni-univalent type** as  $KCl$ , has the highest ionization, averaging about 80–85 per cent. As the valence of the metallic and non-metallic portion increases, the ionization in general decreases. When the concentration is quite low, it is not far from the truth to say that the ionization is approximately complete. There are striking exceptions, however, to the general rules, as can be seen with certain salts of mercury.

The calculation of ionic concentrations from per cent ionization data is as follows: Suppose we wish to calculate the total  $OH^-$



concentration represented by  $[\text{OH}^-]$ , in a  $0.1n$  KOH solution. We find from the ionization table that the per cent ionization is 91.00. Then,  $0.1n \times 0.91 = 0.091n$  and is the actual concentration of KOH that has been ionized. Since a  $n$  KOH solution contains  $n \text{ OH}^-$ , in this example, the concentration of  $[\text{OH}^-] = 0.091n$ . It is understood in this example that the unit of ion measurement is the amount of ionic substance resulting from the ionization of one formula weight of OH, just as the unit by which the KOH concentration is determined is a formula weight of KOH.

There is a point that may give rise to confusion when a bivalent ion is concerned. A  $0.1n$  solution of  $\text{ZnCl}_2$  ionizes 73 per cent. Since Zn is bivalent this corresponds to a  $0.05m$  solution, and  $0.05m \times 0.73 = 0.0365m$  actually in an ionized condition.  $\text{ZnCl}_2 = \text{Zn}^{++} + \text{Cl}^- + \text{Cl}^-$ . Now, if  $0.0365m$  is the concentration of the ionized  $\text{ZnCl}_2$ , then each ion is present in the same concentration. That is, the concentration of  $\text{Zn}^{++}$  ion is  $0.0365m$  and each of the two chloride ions has the same concentration. The total chloride-ion concentration is, therefore,  $2 \times 0.0365m$ , or  $0.073m$ . In the latter case it is really the concentration of all of the chloride ion in terms of unit formula weight of Cl. In expressing ion concentrations, a mole of chloride ion is one formula weight of  $\text{Cl}^-$  and not  $\text{Cl}_2$ , which is customarily involved when dealing with the gas. A molecule is here used in the original sense of a particle, and in ionization considerations  $\text{Cl}^-$ , and not  $\text{Cl}_2$ , is the ultimate particle.

**Electrical conductivity** and **chemical activity** increase as the degree of ionization increases, so that the data obtained from one of these sources can be used to forecast the action in the other two fields. As an example, suppose we take  $0.1m$  HCl. This solution conducts the current well, and from several independent sources we know that it is a highly ionized acid. In our chemical reactions we have selected this acid as one of the desirable ones whenever high acidity is necessary. If, however, dry HCl is dissolved in dry toluene, no ionization occurs and the solution will not conduct the current or react as an acid. Very frequently mixtures of substances are prevented from reacting by being kept dry. Baking powders and Seidlitz powders are examples.

A change in temperature will change the degree of ionization, although the actual variation is small. The following table will give some idea of the changes involved:

TABLE V  
CHANGE OF DISSOCIATION WITH TEMPERATURE \*

Electrolyte	Percentage Dissociation					
	18°	100°	156°	218°	281°	306°
HCl	93.2	89.7	87.2	82.5	.....	60
KCl	87.3	82.6	79.7	77.3	72	64
NaCl	85.7	83.2	81.2	77.7	69	63
AgNO <sub>3</sub>	83.3	80.2	75.8	70.8	60	57
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	81.1	77.6	75.6	68.5	.....	.....
K <sub>2</sub> SO <sub>4</sub>	73.2	64.8	58	45	31	23
Ba(NO <sub>3</sub> ) <sub>2</sub>	70.1	66.9	62	53	38	.....
MgSO <sub>4</sub>	45.5	31.9	19	7	.....	.....
CH <sub>3</sub> CO <sub>2</sub> H	1.50	1.17	0.82	0.46	.....	0.14

\* Taken from Creighton and Fink's "Electrochemistry," John Wiley & Sons, Inc., New York, 1928, vol. I, p. 107.

It has been determined that as a rule **ionization is a slightly exothermal reaction**, so that, by applying Van't Hoff's Law, an increase in temperature should decrease the per cent ionization.

The actual number of ions present in a solution when the temperature is changed involves more than the change of ionization with the temperature. We have seen that the solubility of a substance is usually increased by an increase in temperature. If, then, the solution becomes more concentrated at the higher temperature, the per cent ionization will be decreased from that cause alone. Add to this decrease a slight additional decrease due to the exothermic type of reaction and it can be seen that the total per cent ionization will be materially lessened. As we have previously stated, however, the total number of ions will be increased on account of the greater number of dissolved molecules that are present. If an increase in temperature decreases the solubility of the substance, the solution will be less concentrated, and the per cent ionization will be increased from both the standpoint of concentration of the solution and Van't Hoff's Law. The actual number of ions present will require a numerical calculation to determine whether there has been an increase or a decrease.

The ionization of water is an exception to the rule that per cent dissociation is decreased with a rise in temperature. The ionization of water is very sensitive to temperature changes and increases rapidly as the temperature rises. Numerical dissociation values are given in the section on hydrolysis.

Although the most common solvent is water, it must be remembered that there are other liquid solvents, as alcohol, carbon bisulfide, ether, chloroform and carbon tetrachloride, and that the ionization relationships must be determined for each particular solvent.

The presence of another electrolyte will also change ionization values, because there is a change of conditions just as though another solvent were used. In order not to introduce too many complications in our problem work, we shall disregard the effect on ionization of the presence of other electrolytes.

**Summary.**—When electrolytes are dissolved in suitable solvents they are subdivided into ions, which are atoms or groups of atoms carrying electrical charges. By the law of electrical equivalence we find that the plus and minus charges on ions from one molecule are equivalent in number.

The passage of an electric current through a solution of an electrolyte is accomplished by means of the ions present. In electrolysis ions are separated by the flow of current; the plus ion, going to the minus electrode, or cathode, is named a cation, and the minus ion is correspondingly known as the anion.

Ions move at a relatively slow and independent rate, with  $H^+$  and  $OH^-$  having the greatest velocities.

A solution when colored owes its color to the presence of certain colored molecules or ions.

Ionization is increased by dilution but the actual number of ions per unit volume is greatly decreased.

The extent of ionization is expressed in terms of per cent ionization and the strength of an acid or base depends upon the amount of ionization. Salts are, as a rule, highly ionized. The concentration of ions is best expressed in gram-ions which is less confusing than moles when applied to ion concentrations.

The electrical conductivity of a solution, the degree of ionization and the chemical activity vary at the same rate.

An increase in temperature may increase the total number of ions present by increasing the solubility of the electrolyte, but the



Two views of one of the research laboratories of the Eastman Kodak Co., Rochester, N. Y. A careful examination of pictures of commercial research laboratories will reveal "how the expert does it."



per cent ionization is, as a rule, decreased. The ionization of water is an exception.

Although water is the most common solvent there are many others, and each has its own power of causing ionization.

The presence of another electrolyte affects ionization.

## EXERCISES

1. In tabulated form, show the ions with the correct charges that result from the dissociation of the following electrolytes:  $\text{Na}_2\text{SO}_4$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{BiCl}_3$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{Na}_3\text{AsO}_3$ ,  $(\text{BiO})_2\text{SO}_4$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{H}_2\text{S}$ . *Handwritten notes:  $\text{H}^+$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{Na}_3\text{AsO}_3$ ,  $(\text{BiO})_2\text{SO}_4$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{H}_2\text{S}$ .  $2\text{H}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ ,  $\text{Bi}^{3+}$ ,  $\text{Cl}^-$ .*

2. Make a list of all of the molecules and ions that you know to impart a color to a solution, together with the characteristic color. Do not destroy this list but complete it as you proceed with your analytical work.

3. If sulphuric acid is 61 per cent ionized in 0.1*n* solution, what is the concentration of  $[\text{H}^+]$  in gram-ions per liter? (The ionization into  $2\text{H}^+$  and  $\text{SO}_4^{2-}$  is referred to.) *Handwritten:  $0.61 \times 0.1 = 0.061 \text{ conc. of } (\text{H}^+)$*

4. How many times greater is the concentration of  $[\text{OH}^-]$  in a 0.1*n* NaOH solution than in the same concentration of  $\text{NH}_4\text{OH}$ ? *Handwritten:  $0.134 \times 0.1 = 0.0134$*

5. Will 50 cc. of 0.1*n* NaOH neutralize the same amount of acid as 50 cc. of 0.1*n*  $\text{NH}_4\text{OH}$ ? Give a full explanation. *Handwritten: Yes, as it is a weak base.*

6. Draw a curve for NaCl from the table showing the relation of per cent ionization with concentration, and approximate the ionization for a concentration of 0.05*n*. *Handwritten: ionization curve*

7. From the shape of the curve in Exercise 6, how does the concentration vary with the dilution?

## CHAPTER III

### MOLECULAR EQUILIBRIUM

#### EQUILIBRIUM AND REVERSIBLE REACTIONS

Chemical equilibrium has the same fundamental characteristics as any other type of equilibrium. Take for example, a spring balance in which the pointer is at rest and at zero. The coiled spring is stretched a small amount by the weight of the suspended hook or pan. There are two opposing forces in action, that of the pan, pulling down, and that of the spring, exerting a force in the opposite direction. We say that the balance is in equilibrium because it is at rest, and that rest is brought about by the presence of certain conditions in a pair of opposing tendencies or forces. If the balance rest were caused by the pointer sticking somewhere we should not consider it to be in a state of equilibrium. The pointer must be free to move. One consideration in the study of an equilibrium that is generally overlooked is the fact that during the establishment of an equilibrium one or both of the opposing forces must vary in intensity.

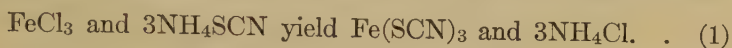
To consider the balance again: before the pan was hung on the lower end of the spring there was no upward pull of the spring. The pan was being pulled down by a constant gravitational force, but not on the spring. The two opposing tendencies had not got together as yet; one, in fact, had not been created. Now as the pan is attached to the spring and is allowed to descend, the spring opposes this constant pull of gravity and, by gradually increasing its upward pull as it is further distorted, it finally brings the pointer to rest. An equilibrium has been established. It can readily be seen that if we start with two unequal opposing forces no equilibrium can be established without an adjustment of at least one of the forces. Unless the spring gradually increased its upward pull it would be stretched by the pan without limit, space permitting.

At equilibrium both forces are still in operation. In our experiment, cut the spring or suddenly remove the pan, and this fact soon becomes evident.

A third characteristic of an equilibrium is that any modification of either force will upset the point of balance, and the two opposing tendencies will set about to establish another point of equilibrium. A weight added to the pan or a tightening of the adjustment on the spring will produce these results.

Another consideration is also worth noting in this physical equilibrium. The time it takes to establish the equilibrium has nothing to do with establishing the point of equilibrium. The pan can be lowered with its weight slowly or rapidly. The point of rest will be the same.

Now, transferring our attention to the chemical idea of equilibrium, suppose we have a reaction between ferric chloride and ammonium thiocyanate as represented by the following equation:



There is a reaction tendency between the first two substances to form the second two substances. This reacting system is said to be homogeneous because no precipitate or gas is formed and the initial and resultant solutions are mutually miscible. It is found, however, that if we start another reaction by using ferric thiocyanate and ammonium chloride they will react, forming ferric chloride and ammonium thiocyanate. We can then write a second equation:



In other words, each pair of substances will produce the other pair if used in two independent and initial reactions. It is evident, then, that in our original equation involving ferric chloride and ammonium thiocyanate, just as soon as the reacting tendency of the substances of the first member produces some of the substances of the second member, a tendency will be set up which will oppose that of the first member. We have stated that no equilibrium will be established unless at least one of the opposing tendencies can vary. In this reaction both of the tendencies vary because, just as soon as the substances in the first member begin to be used up in forming the substances of the second member, the reaction tendency of the first member decreases in intensity or

activity. Correspondingly, that of the second member is started and begins to increase.

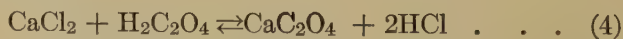
At equilibrium then, just what is the condition? In the first place, there is less of the substances of the first member. There is also a certain amount of the substances of the second member present, and each pair of substances is being formed at the same rate. The pair of **simultaneous reactions**, which is known as a **reversible reaction**, can now be combined and rewritten with a double arrow:



The phrase "reversible reaction" must never imply what the words literally mean, the actual reversal of either of the two reactions involved in the equation.

The two reactions are going on continuously and each in its original direction. The only change is in the rate, until the equilibrium has been established. Another question that arises is this: How much of the original substances will be left at equilibrium, or, in other words, where will the equilibrium point be? It has been determined that the location of this equilibrium point depends upon the chemical characteristics of all of the reacting substances as well as upon the concentrations used. Since the chemical characteristics are in part determined by the temperature, and with gases by the pressure, it is necessary to have a very definite set of substances and conditions present to establish an equilibrium point at a desired position. Viewing the matter from a different angle, the equilibrium point can be displaced by the slightest change of conditions.

The majority of reactions are to a greater or less extent reversible, even when a precipitate is formed. No precipitate is absolutely insoluble in the solution present in the reaction, and this amount held in solution will react and continue an opposing reaction. The reaction between calcium chloride and oxalic acid will serve as an example:



In a side test it can be established that calcium oxalate is soluble in hydrochloric acid. This shows that in the above reaction the calcium oxalate formed is in two states, a portion existing as a precipitate, and another portion present in solution in the hydro-



chloric acid. We have, then, calcium oxalate in solution reacting with hydrochloric acid, tending to form the original substances. The reason why all of the calcium oxalate does not dissolve in the acid is that there is not sufficient acid. In the side test you probably used a small amount of calcium oxalate and an excess of acid. For a high yield, then, there must be very little opportunity for the product desired to be kept in the reversible reaction by solution, pressure or any other circumstance.

**Summary.**—An equilibrium is established when two opposing tendencies or forces have been varied until they are equal. The two forces are still in operation and, if the equilibrium is disturbed, it will necessitate a readjustment of the forces to reestablish equilibrium.

An equilibrium can be approached from either side of the point of equilibrium.

A reversible reaction is in reality a pair of reactions that oppose each other and will finally reach a state of equilibrium by the variation in the concentrations of reacting substances.

The equilibrium point is only constant when the conditions are constant.

A double arrow,  $\rightleftharpoons$ , indicates a reversible reaction.

### EXERCISES

1. A reversible reaction cannot result unless the products are kept together for reaction. Make a list of several methods of removing one of the products so that the reaction will be practically irreversible.

2. In the equation  $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + 2\text{Cl}_2$ , are we to infer that equilibrium is established when one-half of the HCl is used up? Explain in detail.

3. Two volumes of  $\text{H}_2$  and one volume of  $\text{O}_2$  are found to be present in an enclosed vessel, and the amount of each remains unchanged throughout a long period of time. Is this an example of an equilibrium?

4. If we are given the reaction,  $\text{AB} + \text{CD} = \text{AD} + \text{CB}$ , and a precipitate is formed, how are we to determine if the reaction is to any degree reversible?

5. How may an increase in temperature promote reversibility?

### DISPLACEMENT OF EQUILIBRIA AND THE LAW OF MOLECULAR CONCENTRATION

In the last section the conditions for a chemical equilibrium were discussed. We shall now look into the displacement of the equilibrium point. A very interesting experiment performed by

Gladstone in 1855 throws much light upon the subject and again involves the reaction:

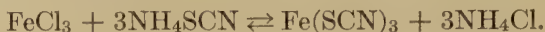


Plate I, A, shows a reddish solution resulting from mixing two dilute solutions of  $\text{FeCl}_3$  and  $\text{NH}_4\text{SCN}$ . The color is due to the red molecules of  $\text{Fe}(\text{SCN})_3$ . By dividing the red solution into two parts and adding to one some  $\text{FeCl}_3$  and to the other some  $\text{NH}_4\text{SCN}$ , it is found that in both cases the color is deepened as shown in B, thus proving that the equilibrium point has been moved to the right. Now, by adding some solid  $\text{NH}_4\text{Cl}$  to either portion containing the deepened color, the color can be almost entirely discharged as is shown in C. This would indicate that the equilibrium point has been moved almost completely to the left.

It is evident that by increasing the number of reacting molecules in either member of the equation the speed of reaction of that particular member is increased and the equilibrium point is moved toward the other member. **Guldberg and Waage**, in 1867, gave a formal statement of the effect of varying the number of reacting molecules upon the displacement of an equilibrium. They proposed that the amount of chemical reaction depends upon the active masses present. The expression "active masses" is an unfortunate one because it is evident that not the masses present but the molecules per volume of solution is the important thing. It follows, then, that instead of the law of mass action, we are more particularly concerned with the **Law of Molecular Concentration**.

A clearer conception of the equilibrium relationship may be obtained from a mathematical presentation of the facts. Suppose that the substances AB and CD are in equilibrium with the substances AD and CB. At a certain constant temperature we have, according to the molecular concentration law.

$$v_1 \propto [\text{AB}][\text{CD}], \quad . . . . . (5)$$

where  $v_1$  = speed of reaction of first member;

[ ] = total concentration of substance enclosed and is expressed in any convenient unit.

Expressing (5) as an equation:

$$v_1 = K_1[\text{AB}][\text{CD}], \quad . . . . . (6)$$



where  $K_1$  is a constant necessary to change a variation to an equation and is determined by an experiment in which the actual speed of reaction of AB and CD is investigated.

Similarly:

$$v_2 = K_2[AD][CB]. \quad . . . . . (7)$$

At equilibrium the velocities of the two reactions are equal; then:

$$K_1[AB][CD] = K_2[AD][CB] \quad . . . . . (8)$$

Putting this in the form of a proportion:

$$\frac{K_1}{K_2} = \frac{[AD][CB]}{[AB][CD]} \quad . . . . . (9)$$

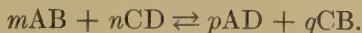
But, since a constant divided by a constant equals a constant:

$$K_{eq} = \frac{[AD][CB]}{[AB][CD]} \quad . . . . . (10)$$

$K_{eq}$ , the **equilibrium constant**, shows the mathematical relationship that exists between the product of the concentrations of the substances in the first member and the product of the concentrations of the substances in the second member.

The relationship just discussed constitutes the **Law of Chemical Equilibrium** and is erroneously referred to as the Mass Law. The Mass Law or, more correctly, the Law of Molecular Concentrations, has to do with the speed of any reaction, and all reactions do not run to equilibrium.

The general expression involving coefficients other than 1 for the reacting substance is represented by:



$$K_{eq} = \frac{[AD]^p [CB]^q}{[AB]^m [CD]^n} \quad . . . . . (11)$$

The concentration of each substance is expressed in terms of unit formula weight.

In expressing equilibrium ratios there is a lack of uniformity in the matter of deciding which concentrations should be written in the numerator and which in the denominator. It is perfectly correct to view an equilibrium reaction from either side, and funda-

5000

mentally it is correct to place the concentration of the right-hand member in either numerator or denominator. To avoid unnecessary confusion, however, there should be some uniformity of expression. In writing a similar ratio for ionic equilibria, the ions that constitute the second member are always placed in the numerator of the equilibrium ratio. We shall at least be uniform by doing the same with molecular ratios.

The equilibrium constant is not the point of equilibrium. We found that the point of equilibrium can be displaced one way or the other by varying the concentrations of the substances involved. This point indicates how far the reaction had progressed one way or the other when equilibrium was established. The equilibrium constant, however, is, as the name implies, a fixed number and is an unchanged ratio as long as the same substances are used (in any concentration) and the temperature is kept the same.

To illustrate how the constant is applied, suppose we start with 1 mole each of AB and CD. At equilibrium it is found by analysis that there still remains  $\frac{1}{3}$  mole each of AB and CD and that  $\frac{2}{3}$  mole each of AD and CB are present.

Substituting in (11):

$$\frac{(ad)+(cb)}{(ab)+(cd)} = \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = 4 = K_{eq.}$$

$$AB + CD \longrightarrow AD + CB$$

Now suppose, for example, we wish to displace the equilibrium point far to the right, and, to give a practical turn to the problem, let us assume that we are making AD by the action of an expensive substance AB, and a cheap substance CD. Naturally we wish to bring into reaction as much of AB as possible. We have seen that if we use one mole of each or multiples of this ratio, one-third of AB will remain at equilibrium. Suppose, however, that we use a large excess of the cheap substance CD, say ten times as much as called for by a molecular ratio, and substitute in the formula.  $x$  is to represent the moles of AB and CD transformed, as well as the moles of AD and CB formed. Then:

$$\frac{x^2}{(1-x)(10-x)} = 4.$$

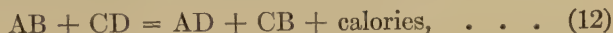
Solving,  $x = 13.7$  or 0.98. Evidently, 13.7 moles cannot be transformed because we only started with one mole of AB; there-



fore, 0.98 mole is the correct answer. This indicates that practically all of AB was used.

A better method to obtain a large yield of AD and, in fact, to use up all of AB, is to have an excess of CD and also to remove AD from the right-hand member as fast as formed. No reversible reaction is thus allowed to develop. A further discussion of this principle will be given in a later section.

The factors that change the value of  $K_{eq}$  for the same reacting substances are the temperature and, with gases, the pressure. If a pressure change on solutions changed the solubility of the substances in solution to any reasonable extent, then pressure would have to be considered in connection with the equilibrium of solutions. This is not the case, however. Just how temperature shifts the value of  $K_{eq}$  is summarized in **Van't Hoff's Law** which states that when a reaction that has come to equilibrium has the temperature increased the equilibrium will be displaced in such a direction that heat is absorbed. For example, if heat is added to an exothermal reaction where:



the equilibrium will be displaced to the left.

An increase in temperature would have no effect upon  $K_{eq}$  if it increased the speed of both reactions in the equilibrium by the same per cent; the equilibrium would merely be established in less time than before heating. This is not the case, however, and heating has the same effect as introducing another pair of substances, with new reacting tendencies, into the reaction.

The **Le Chatelier Law** is more general and applies to any stress brought to bear upon a system in equilibrium. It states that when a system has come to equilibrium and any stress is brought to bear upon it, there will be a shift in the equilibrium that will tend to undo this stress.

When the Law of Molecular Concentration is experimentally tested it is found to hold only within certain limits. This law takes into consideration the number of molecules and makes no allowance for any change in the reaction characteristics brought about by a change in concentration, or the particular chemical reacting strength of the substance itself. For example, 0.025*m* solutions from any source will, upon mathematical substitution in the formula, give the same reacting values. Experimentally the

law is found to hold true only with weak electrolytes and even then in moderate concentrations only.

It is evident that there are many contributing factors that determine the speed of a reaction, especially in high concentrations. In other words, the actual molecular concentration must be corrected by a coefficient in order to represent more exactly the **reacting activity** of the substance. The **activity coefficient** and the activity of the molecular concentrations are represented in the following equation:

$$a = \alpha C,$$

where  $a$  = molecular activity,  $\alpha$  = the activity coefficient, and  $C$  = concentration in moles.

Fortunately, in qualitative analysis, where precipitates are concerned, the actual amount of the precipitate which is dissolved gives such a dilute solution that we shall not be concerned further with activities and their coefficients.

**Summary.**—The point of equilibrium in a reversible reaction that has come to equilibrium can be displaced one way or the other by varying the concentrations of the reacting molecules in the two individual reactions.

This effect of molecular concentration upon the speed of a reaction is embodied in the Law of Molecular Concentration as specifically proposed by Guldberg and Waage in 1867. The law states that the speed of a chemical reaction is proportional to the molecular concentrations of the reacting substances.

The equilibrium constant,  $K_{eq}$ , mathematically expresses the ratio of the products of the molecular concentrations of both members of a reversible reaction and is a most convenient method for studying the effect of the so-called Mass Law.

The equilibrium constant remains unchanged so long as the temperature is constant.

Where temperature is a constant and the reacting substances are the same, any of the concentrations can be altered without affecting the value of  $K_{eq}$ .

Where  $K_{eq}$  is known, one of the molecular concentrations can be calculated if the remaining ones are given.

The value of  $K_{eq}$  is different for different reacting substances.

The activity coefficient  $\alpha$  is a correction to be applied to the actual molecular concentration to give more accurately the real

reacting concentration, or activity, of a substance. Activity =  $\alpha C$ .

## EXERCISES

1. Calculate  $K_{eq}$  from the following: One mole each of AB and CD is found at equilibrium to be reduced by 80 per cent each in concentration. The products are AD and CB and are present at equilibrium in equal amounts.  $K_{eq} = 1$

2. If a certain increase in temperature increases  $K_{eq}$  by 15 per cent, recalculate the amounts of the four substances present at equilibrium.

3. Using the values in Exercise 1, show the effect of doubling the concentrations of AB and CD.

$$\frac{4 + 4(1 - x)}{(1 - x)(1 - x)} = 18.4$$

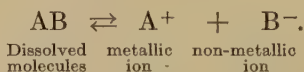
$$\frac{4 + 4(1 - x)}{(1 - x)(1 - x)} = 16$$

## CHAPTER IV

### IONIC EQUILIBRIUM

#### IONIC EQUILIBRIA AND IONIZATION CONSTANTS

When we were considering the characteristics of ionization it was stated that a portion of the dissolved molecules of any electrolyte broke up into smaller bodies called ions. It is also true that these ions tend to recombine, forming dissolved molecules. If the speeds of these two reactions are proportional to the concentration of dissolved molecules on the one hand, and to the concentration of ions on the other, we have again the essential characteristics for another reversible reaction which can attain a state of equilibrium. The characteristics of this equilibrium are identical with those already considered with molecular concentrations and can be expressed by the equation:



An equilibrium constant for this reversible reaction would be:

$$K_{eq} = \frac{[A^+][B^-]}{[AB]}. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This particular equilibrium constant, which involves ionization, is generally known as the **ionization constant**<sup>1</sup> and will be referred to in this manner hereafter. However, it should be constantly kept in mind that it is essentially an equilibrium constant.

To show how the ionization constant is expressed for an acid, we shall first use acetic acid because it is a weak acid and is **mono-basic**.

<sup>1</sup> The ionization constants, as a special development of the molecular equilibrium constants, were first presented by Ostwald in his Dilution Law investigations. *Zeitschr. physikal. Chem.* **2**, 36 (1888); **3**, 170 (1889).



The reversible reaction is expressed by:



and the ionization constant equals:

$$K_{\text{ion}} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \quad (14)$$

As with all equilibrium constants, the temperature must be unchanged and the value of  $K_{\text{ion}}$  is secured from data in which all of the factors in the fraction are experimentally determined. All of the concentrations except one can now be varied at will and the remaining factor obtained by calculation. Dealing with a concrete case, let us take the data for the ionization of acetic acid. The per cent ionization of a  $0.1n$  solution at about room temperature is 1.34. Now,  $0.1n \times 0.0134 = 0.00134n$ , the concentration of acetic acid that actually ionizes. This concentration also represents  $[\text{H}^+]$  and  $[\text{CH}_3\text{CO}_2^-]$ . The un-ionized portion is, therefore,  $0.09866n$  and, substituting in the formula for  $K_{\text{ion}}$ :

$$K_{\text{ion}} = \frac{0.00134 \times 0.00134}{0.09866} \quad (15)$$

$$= 0.000018.$$

Let us now, with this value for  $K_{\text{ion}}$ , proceed to calculate the  $[\text{H}^+]$  in a  $0.02n$  solution and also the per cent ionization. At this concentration we shall assume the ionization is  $x$  and we have:

$$\frac{x^2}{0.02 - x} = 0.000018, \quad (16)$$

whence,

$$x^2 = (0.02 - x)(0.000018),$$

$$= 0.00000036 - 0.000018x,$$

or

$$x^2 + 0.000018x = 0.00000036.$$

Solving,

$$x = 0.000591n \text{ or } -0.000609n.$$

The second value, being negative, is not used.

Since  $x$  is very small, the algebraic solution can be much sim-

591  
609  
1200

plified by assuming that 0.02 remains practically constant. We then have:

$$\frac{x^2}{0.02} = 0.000018, \quad . . . . . (17)$$

whence,

$$x^2 = 0.00000036,$$

or

$$x = 0.0006n.$$

If we started with  $0.02n$  acetic acid and  $0.0006n$  ionized, then  $0.02 - 0.0006 = 0.0194n$ , or the un-ionized part. The per cent ionized will be:

$$\frac{0.0006}{0.02} \times 100 = 3.$$

It is well to note that the effect of dilution from  $0.1n$  to  $0.02n$  has been to increase the per cent ionization from 1.34 to 3.

Where **polybasic acids** or **polyacid bases** are involved, it should be remembered that  $K_{\text{ion}}$  must refer to a certain, particular ionization just as we noted in giving the per cent ionization in Table IV. It is well to add a word of caution at this point, namely, that  $K_{\text{ion}}$  does not represent mathematically the per cent ionization.  $K_{\text{ion}}$  and the per cent ionization are developed in a somewhat parallel manner with different types of ionization but their mathematical meaning and values are very different. The first gives a mathematical relationship between the product of concentrations of the ions formed and the concentration of the un-ionized substance remaining, while the per cent ionization relates the amount ionized to the original concentration taken and has nothing to do with any relation existing within the ionized portion.

The expressions for  $K_{\text{ion}}$  for carbonic acid,  $\text{H}_2\text{CO}_3$ , are as follows:

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}, \quad . . . . . (18)$$

where  $K_1$  is the primary ionization constant with a value<sup>2</sup> of  $0.063$ , and:

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}, \quad . . . . . (19)$$

<sup>2</sup>  $0.063$  is a conventional method of expressing decimal values and equals  $0.0000003$ .

where  $K_2$  is the secondary ionization constant with a value of  $0.0_{10}7$ .  $K_{\text{ion}}$ , the ionization constant involving all the ionizations, is shown by:

$$K = \frac{[\text{H}^+]^2 [\text{CO}_3^{=}]}{[\text{H}_2\text{CO}_3]} \cdot \cdot \cdot \cdot \cdot \cdot (20)$$

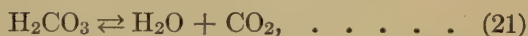
The value for  $K_{\text{ion}}$  is given in many tables as  $0.0_{6}3$ , the same as for  $K_1$ , because  $K_2$  represents an insignificant value. In solving numerical problems involving a very weak secondary or tertiary ionization, it is not customary to raise the  $[\text{H}^+]$  to the second or third power because the effective ionization is in reality that of a monobasic acid.

Where tables are used in which  $K_{\text{ion}}$  values for salts and strong acids and bases are given, it must not be inferred that these values are real ionization constants, that is, that they remain unchanged during a variation of concentration of electrolyte. They are in reality only numerical values which have been calculated for the particular concentration given and are usually enclosed in parenthesis. For example, in a  $0.1n$   $\text{HCl}$  solution the numerical value for

$$\frac{[\text{H}^+] [\text{Cl}^-]}{[\text{HCl}]} = 1.$$

This pseudo  $K_{\text{ion}}$  cannot be used in calculations involving  $0.05n$  solutions of  $\text{HCl}$ .

With carbonic acid and ammonium hydroxide a further development of ionization takes place because the unstable compounds  $\text{H}_2\text{CO}_3$  and  $\text{NH}_4\text{OH}$  are in equilibrium with the products of instability as well as with the immediate ions. These two equations will illustrate the point:



The denominator for the ionization constant, as given in the tables, contains the total carbonic acid as well as the  $\text{CO}_2$ . The value for  $K_{\text{ion}}$  for  $\text{NH}_4\text{OH}$  is calculated in a similar manner and will be presented in full in a later section.

TABLE VI

IONIZATION CONSTANTS AT APPROXIMATELY 18° FOR 0.1*m* SOLUTIONS OF THE MORE COMMON WEAK ACIDS AND BASES USED IN QUALITATIVE ANALYSIS

<i>Acids</i>	<i>Equilibrium Ratio</i>	<i>K ion</i>
Hydrogen sulfide	$[H^+][HS^-]/[H_2S]$	0.079
	$[H^+][S^{2-}]/[HS^-]$	0.0141
Arsenious	$[H^+][H_2AsO_3^-]/[H_2AsO_3]$	0.06
Arsenic	$[H^+][H_2AsO_4^-]/[H_2AsO_4]$	0.05
Phosphoric	$[H^+][H_2PO_4^-]/[H_2PO_4]$	0.01
	$[H^+][HPO_4^{2-}]/[H_2PO_4^-]$	0.062
	$[H^+][PO_4^{3-}]/[HPO_4^{2-}]$	0.0124
Hydrocyanic	$[H^+][CN^-]/[HCN]$	0.067
Carbonic	$[H^+][HCO_3^-]/[H_2CO_3]$	0.063
	$[H^+][CO_3^{2-}]/[HCO_3^-]$	0.0167
Acetic	$[H^+][CH_3CO_2^-]/[CH_3CO_2H]$	0.018
Oxalic	$[H^+][HC_2O_4^-]/[H_2C_2O_4]$	(0.038)
	$[H^+][C_2O_4^{2-}]/[HC_2O_4^-]$	0.05
Boric	$[H^+][H_2BO_3^-]/[H_3BO_3]$	0.037
<i>Bases</i>		
Barium hydroxide	$[Ba^{++}][OH^-]^2/[Ba(OH)_2]$	(0.03)
Ammonium hydroxide	$[NH_4^+][OH^-]/[NH_4OH]$	0.018
Water *	$[H^+][OH^-]/H_2O$	0.01811

\*  $H-O-H$  can be considered as a very weak acid or base since it contains both  $H^+$  and  $OH^-$  upon ionization. The per cent ionized at 18° has already been given as 0.000000142.

An interesting series of calculations showing the constancy of  $K_{ion}$  for a weak electrolyte and its inconstancy for a strong electrolyte can be made by substituting the per cent ionization data at two concentrations in the expressions for  $K_{ion}$ .

A 0.01*m* acetic acid solution is ionized 4.17 per cent and 0.1*m* is ionized 1.34 per cent. Substituting for  $K_{ion}$  at 0.01*m* concentrations:

$$\begin{aligned}
 K_{ion} &= \frac{[H^+][Ac^-]}{0.01 - (0.01 \times 0.0417)} \\
 &= \frac{(0.000417)^2}{0.009583} \\
 &= 0.00001813.
 \end{aligned}$$

Similarly, for 0.1*m* concentration,

$$K_{ion} = 0.0000182.$$

$$x^2 = .097$$

$$x = .00008361$$

$$.00008361 \times 100 = .008361$$

$$x^2 = .013$$

$$x = .0001732$$

$$.0001732 \times 100 = 17.32$$




The two values for  $K_{\text{ion}}$  in acetic acid show the constancy of the value and also show how the concentrations of a weak electrolyte can be varied throughout a wide range without disturbing this equilibrium constant.

Making another set of calculations for HCl at the same two concentrations as we used for acetic acid, we find that at 0.01*m* the acid is ionized 97.2 per cent and at 0.1*m* it is ionized only 92.0 per cent. Substituting for 0.01*m*:

$$K_{\text{ion}} = \frac{(0.01 \times .972)^2}{0.01 \times 0.028} \\ = 0.337,$$

while for 0.1*m*:

$$K_{\text{ion}} = \frac{(0.092)^2}{0.008} \\ = 1.06.$$

Remember these calculations later when we are speaking of the limitations of the Mass Law. 

**Summary.**—Since dissolved molecules are in equilibrium with the ions resulting from their fractional dissociation, an equilibrium constant  $K_{\text{ion}}$ , can be used to express the equilibrium ratio.

$K_{\text{ion}}$  is only a constant for an individual molecular dissociation at a definite concentration and temperature.

Unless otherwise stated, the concentration is assumed to be 0.1*n*.

$K_{\text{ion}}$  is not per cent dissociated, but each of these values can be calculated from the other.

It is assumed that  $K_{\text{ion}}$  represents the ionization value that is given for the entire molecular ionization, if the specific type is not mentioned.

Ionization constants calculated from ionization data involving the same two concentrations of a weak acid and a strong acid show that there is constancy only with the weak acid. So-called ionization constants for strong electrolytes are of little value.

### EXERCISES

1. Calculate the per cent ionization from the following  $K_{\text{ion}}$  values: acetic acid, 0.0418; boric acid, 0.047; carbonic acid, primary, 0.043.

2. If the  $K_{\text{ion}}$  values for the primary and secondary ionizations of oxalic acid are 0.038 and 0.045, respectively, what is the total  $[\text{H}^+]$  in this 0.1*n* solution?

3. Using values given in the table of per cent ionizations, calculate  $K_{\text{ion}}$  for the following:  $\text{H}_2\text{SO}_4$ ;  $\text{H}_3\text{PO}_4$ , primary;  $\text{H}_2\text{S}$ , primary;  $\text{Ba}(\text{OH})_2$ ;  $\text{K}_2\text{SO}_4$ .

## PLATE I

**A.** A solution resulting from the addition of two drops of KSCN to a very dilute solution of  $\text{FeCl}_3$ . The color, usually characterized as blood-red, is due to the dissolved molecules of  $\text{Fe}(\text{SCN})_3$ . This is an important test for both  $\text{Fe}^{+3}$  and  $\text{SCN}^-$ .

**A-B-C.** This series of solutions illustrates the law of molecular concentration in the reaction:



Starting with a certain concentration of  $\text{Fe}(\text{SCN})_3$  in **A**, the color is made more intense, as shown in **B**, by adding more  $\text{FeCl}_3$  or KSCN; the equilibrium point is moved to the right. In **C**, solid KCl has been added and the equilibrium point has been correspondingly moved to the left as shown by the removal of most of the color. The color cannot be completely removed by this method.

**D.** A solution containing a light-yellow precipitate of  $\text{BaCrO}_4$ . If  $\text{PbCrO}_4$  is precipitated from concentrated solutions, it may be nearly white at first and gradually passes through this shade of yellow, finally becoming the color of **E**, which is used in pigments as chrome-yellow. The precipitates of  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{S}_5$  are also very light yellow in color.

**E.** The characteristic chrome-yellow precipitate of  $\text{PbCrO}_4$  has been obtained by adding a few drops of  $\text{K}_2\text{CrO}_4$  to a dilute solution of  $\text{Pb}(\text{NO}_3)_2$ . The yellow precipitate of  $\text{CdS}$  is usually darker than that of **D** and lighter than **E**, but the exact shade depends upon the conditions of precipitation.

**F.** This solution shows the effect of adding a few drops of KSCN to water which has been acidified with  $\text{HNO}_3$  but does not contain  $\text{Fe}^{+3}$ . The blood-red color that develops is identical with that of  $\text{Fe}(\text{SCN})_3$ . Warming, however, causes an oxidation reaction to start at the surface of the solution and this gradually passes down through the solution. During this action, brown fumes of  $\text{NO}_2$  are given off and the solution changes to green. This serves as a method to distinguish from the iron test.

**G.** The color of a dilute solution of  $\text{CuSO}_4$ . Reference books state that the color of  $\text{Cu}^{++}$  is blue, but in practice it is difficult to obtain a solution which does not also contain un-ionized molecules of the original salt as  $\text{CuSO}_4$ ,  $\text{Cu}(\text{NO}_3)_2$  and  $\text{CuCl}_2$ . The presence of these molecules in varying degrees of hydration gives a decidedly greenish-blue cast to the solution. A dilute solution of  $\text{CuSO}_4$  is not exactly the same color as one of  $\text{Cu}(\text{NO}_3)_2$  and of the same concentration.

**H.** Sufficient water has been added to a concentrated brown solution of  $\text{CuBr}_2$  to change the color to a dark greenish-brown by the limited formation of cupric ions. Solid KBr is added and the common-ion effect is shown in **I**.

**I.** By the common-ion effect of the  $\text{Br}^-$  from the KBr added in **H**, the  $[\text{Cu}^{++}]$  is reduced to such an extent that the lower part of the solution containing KBr has changed from a greenish-brown to the brown where  $\text{CuBr}_2$  predominates.

**J.** The characteristic deep-blue solution containing the copper-ammonia complex,  $\text{Cu}(\text{NH}_3)_4^{++}$ .

**K.** The light yellow precipitate of  $\text{K}_2\text{PtCl}_6$  which does not darken upon standing.

**L.** The orange-yellow precipitate of  $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$ . If this substance is precipitated rapidly from a concentrated solution it may be as light as  $\text{K}_2\text{PtCl}_6$  when first formed but darkens upon standing.

PLATE I



A



B



C



D



E



F



G



H



I



J



K



L



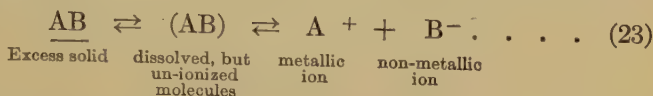


## CHAPTER V

### THE SOLUBILITY-PRODUCT

#### THE SOLUBILITY-PRODUCT PRINCIPLE

One of the most valuable applications of the equilibrium constant in analytical work is in connection with saturated solutions of sparingly soluble substances. Expressing the equilibrium relationships in a saturated solution in equilibrium with an excess of solid:



Writing the value of  $K_{\text{ion}}$ :

$$K_{\text{ion}} = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}] = K_1} \dots \dots \dots (24)$$

Since  $[\text{AB}]$  represents the concentration of the dissolved but un-ionized molecules, the value must be a constant which we will represent by  $K_1$ . Clearing of fractions, we have:

$$K_{\text{ion}} \times K_1 = [\text{A}^+][\text{B}^-] \dots \dots \dots (25)$$

Substituting the constant  $K_{\text{sp}}$ , the solubility-product constant, for  $K_{\text{ion}} \times K_1$ , there results:

$$K_{\text{sp}} = [\text{A}^+][\text{B}^-] \dots \dots \dots (26)$$

In other words, in a saturated solution, the product of the ion concentrations is a constant, and this fact is the basis of the solubility-product principle.

In an unsaturated solution it is possible to determine the concentrations of the ions present, and from this to obtain an ion-product. The product, however, will not be the solubility product that has a constant value, because it has not resulted from ion concentrations in a saturated solution. It follows that  $K_{\text{sp}}$  is the

maximum ion-product that it is possible to obtain from a solution in which the concentration is not greater than in a saturated solution.<sup>1</sup> The solubility product constant is frequently referred to as **the saturation value of the product of ion concentrations.**

To show more clearly the relationship between  $K_{SP}$  and  $K_{ion}$ , we shall use the expression for  $K_{ion}$  for  $AgCl$ :

$$K_{ion} = \frac{[Ag^+][Cl^-]}{[AgCl]}.$$

Silver chloride is very insoluble, the concentration being 0.0<sub>3</sub>15 grams in 100 cc. of solution at 20°. This concentration, expressed in moles, is 0.0<sub>4</sub>105*m*. In a solution so dilute,<sup>2</sup> there is approximately complete ionization, so that the concentration used to express the value of the denominator in  $K_{ion}$  also becomes the value for  $[Ag^+]$  and  $[Cl^-]$  of the numerator. The value, then, for  $K_{SP}$ , is:

$$\begin{aligned} K_{SP} &= [0.0_4105][0.0_4105] \\ &= [0.0_4105]^2 = 0.0_911. \end{aligned}$$

It can be seen that with the substitution of increasingly insoluble substances in  $K_{ion}$ , the value of the denominator approaches zero and that the fraction approaches infinity.

Where a bivalent ion is concerned, the procedure followed is that given in equation (11). For example, using

$$\begin{aligned} PbCl_2 &\rightleftharpoons Pb^{++} + 2Cl^- \\ K_{SP} &= [Pb^{++}][Cl^-]^2 \\ &= 3.9 \times 10^{-2} \times [2(3.9 \times 10^{-2})]^2 \\ &= 3.9 \times 10^{-2} \times [7.8 \times 10^{-2}]^2 \\ &= 3.9 \times 10^{-2} \times 60.84 \times 10^{-4} \\ &= 237.12 \times 10^{-6} = 2.4 \times 10^{-4}. \end{aligned}$$

<sup>1</sup> It will be understood hereafter that the solubility product refers to the saturation constant, and not to any indefinite ion-product.

<sup>2</sup> Recall that a saturated solution is not necessarily concentrated, as may be carelessly inferred. A saturated solution contains the maximum amount that can be held in equilibrium with an excess of solid at a specified temperature. This concentration will be large or small, depending upon the solubility of the substance.

Just as  $K_{eq}$  is a number and does not represent moles or any other unit of concentration, so  $K_{SP}$  is a number and represents a product which in analytical work is used as a number for reference. Any ion-product less in value than  $K_{SP}$  represents an unsaturated solution. An ion-product greater than  $K_{SP}$  denotes a state of supersaturation, and generally the excess will be thrown out as a precipitate. It is also evident that whatever unit of concentration is used in calculating  $K_{SP}$  the same unit must be used in all subsequent work where this series of solubility-product values is employed. The customary series is based upon concentrations expressed in moles. A mole in solubility-product calculations is considered to be a gram-formula weight whether it applies to a molecule or to an ion. Thus a mole of  $Cl^-$  is based upon a gram-atomic weight of  $Cl$  and not upon a gram-molecular weight of  $Cl_2$ . Since solubilities are specific for different dissolved substances, it is evident that each substance will have its individual solubility product.

A more convenient method of expressing small solubility decimals will now be explained before the table of solubility-product constants is presented. The expression  $0.0013$  has been used as an abbreviated form of  $0.00013$ . The same thing, expressed in terms of 10 to the zero power, would be  $0.00013 \times 10^0$ , because  $10^0 = 1$ . Multiplying one factor by 10 and dividing the other by 10 will leave the value of the decimal unchanged. Indicating this operation, we have:

$$\begin{aligned} & [0.00013 \times 10] \left[ \frac{10^0}{10} \right] \\ &= 0.0013 \times \frac{1}{10} \\ &= 0.0013 \times 10^{-1}. \end{aligned}$$

A very convenient and universal method is to express these small decimals in terms of 10 to some negative power, and it is also the rule never to have the coefficient of  $10^{-x}$  contain a numeral portion as large as 10. Therefore, in this example,  $0.0013$  will be pointed off so that  $1.3$  is present as a coefficient, and not  $13$ . The value becomes  $1.3 \times 10^{-4}$ . In this transformation the value of the decimal has not been changed at all because we have in the last step multiplied the first factor by 1000 and divided the second factor by the same amount.

Where this method of expressing solubilities is followed, the relative solubilities of two compounds can be determined at a glance because the one with the larger negative exponent will be the less soluble. However, where the two have the same negative exponent, the one with the larger coefficient is the more soluble.

TABLE VII

SOLUBILITY PRODUCTS FOR THE MORE COMMON PRECIPITATES IN QUALITATIVE ANALYSIS. THE METALS ARE ARRANGED IN THE REVERSE ORDER OF THE ELECTROMOTIVE SERIES AND THE TEMPERATURE IS APPROXIMATELY 18°.

<i>Sparingly Soluble Salt</i>	<i>Ions Involved</i>	<i>Solubility-Product Constant</i>
Ag <sub>2</sub> S	(Ag <sup>+</sup> ) <sup>2</sup> × S <sup>-</sup>	1.6 × 10 <sup>-49</sup>
AgCl	Ag <sup>+</sup> × Cl <sup>-</sup>	1.1 × 10 <sup>-10</sup>
AgBr	Ag <sup>+</sup> × Br <sup>-</sup>	7.7 × 10 <sup>-13</sup>
AgI	Ag <sup>+</sup> × I <sup>-</sup>	0.9 × 10 <sup>-16</sup>
Hg <sub>2</sub> Cl <sub>2</sub>	Hg <sup>+</sup> × Cl <sup>-</sup>	3.5 × 10 <sup>-13</sup>
HgS	Hg <sup>++</sup> × S <sup>-</sup>	4.0 × 10 <sup>-54</sup>
CuBr	Cu <sup>+</sup> × Br <sup>-</sup>	4.1 × 10 <sup>-8</sup>
CuCl	Cu <sup>+</sup> × Cl <sup>-</sup>	1.0 × 10 <sup>-6</sup>
CuI	Cu <sup>+</sup> × I <sup>-</sup>	5.0 × 10 <sup>-12</sup>
CuS	Cu <sup>++</sup> × S <sup>-</sup>	2.0 × 10 <sup>-47</sup>
As <sub>2</sub> S <sub>3</sub>	(As <sup>+3</sup> ) <sup>2</sup> × (S <sup>-</sup> ) <sup>3</sup>	? *
Bi <sub>2</sub> S <sub>3</sub>	(Bi <sup>+3</sup> ) <sup>2</sup> × (S <sup>-</sup> ) <sup>3</sup>	? *
Sb <sub>2</sub> S <sub>3</sub>	(Sb <sup>+3</sup> ) <sup>2</sup> × (S <sup>-</sup> ) <sup>3</sup>	? *
PbCl <sub>2</sub>	(Pb <sup>++</sup> ) × (Cl <sup>-</sup> ) <sup>2</sup>	2.4 × 10 <sup>-4</sup>
PbCrO <sub>4</sub>	Pb <sup>++</sup> × CrO <sub>4</sub> <sup>-</sup>	1.8 × 10 <sup>-14</sup>
PbSO <sub>4</sub>	Pb <sup>++</sup> × SO <sub>4</sub> <sup>-</sup>	1.0 × 10 <sup>-8</sup>
PbS	Pb <sup>++</sup> × S <sup>-</sup>	5.0 × 10 <sup>-29</sup>
SnS	Sn <sup>++</sup> × S <sup>-</sup>	? *
NiS	Ni <sup>++</sup> × S <sup>-</sup>	1.4 × 10 <sup>-24</sup>
CoS	Co <sup>++</sup> × S <sup>-</sup>	3.0 × 10 <sup>-26</sup>
Fe(OH) <sub>2</sub>	Fe <sup>++</sup> × (OH <sup>-</sup> ) <sup>2</sup>	1.6 × 10 <sup>-14</sup>
Fe(OH) <sub>3</sub>	Fe <sup>+3</sup> × (OH <sup>-</sup> ) <sup>3</sup>	1.1 × 10 <sup>-36</sup>
FeS	Fe <sup>++</sup> × S <sup>-</sup>	3.7 × 10 <sup>-19</sup>
CdS	Cd <sup>++</sup> × S <sup>-</sup>	3.6 × 10 <sup>-29</sup>
Zn(OH) <sub>2</sub>	Zn <sup>++</sup> × (OH <sup>-</sup> ) <sup>2</sup>	1.8 × 10 <sup>-14</sup>
ZnS	Zn <sup>++</sup> × S <sup>-</sup>	1.2 × 10 <sup>-23</sup>
Mn(OH) <sub>2</sub>	Mn <sup>++</sup> × (OH <sup>-</sup> ) <sup>2</sup>	4.0 × 10 <sup>-14</sup>
MnS	Mn <sup>++</sup> × S <sup>-</sup>	1.4 × 10 <sup>-15</sup>
HALO <sub>2</sub>	H <sup>+</sup> × AlO <sub>2</sub> <sup>-</sup>	3.7 × 10 <sup>-15</sup>
Mg(OH) <sub>2</sub>	Mg <sup>++</sup> × (OH <sup>-</sup> ) <sup>2</sup>	3.4 × 10 <sup>-11</sup>
MgNH <sub>4</sub> PO <sub>4</sub>	Mg <sup>++</sup> × NH <sub>4</sub> <sup>+</sup> × PO <sub>4</sub> <sup>-3</sup>	2.5 × 10 <sup>-13</sup>
MgCO <sub>3</sub>	Mg <sup>++</sup> × CO <sub>3</sub> <sup>-</sup>	2.6 × 10 <sup>-5</sup>



TABLE VII—Continued

<i>Sparingly Soluble Salt</i>	<i>Ions Involved</i>	<i>Solubility-Product Constant</i>
CaCO <sub>3</sub>	Ca <sup>++</sup> × CO <sub>3</sub> <sup>-</sup>	9.8 × 10 <sup>-8</sup>
CaC <sub>2</sub> O <sub>4</sub>	Ca <sup>++</sup> × C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	2.6 × 10 <sup>-9</sup>
CaSO <sub>4</sub>	Ca <sup>++</sup> × SO <sub>4</sub> <sup>-</sup>	6.2 × 10 <sup>-5</sup>
CaCrO <sub>4</sub>	Ca <sup>++</sup> × CrO <sub>4</sub> <sup>-</sup>	2.3 × 10 <sup>-2</sup>
SrCO <sub>3</sub>	Sr <sup>++</sup> × CO <sub>3</sub> <sup>-</sup>	1.6 × 10 <sup>-9</sup>
SrC <sub>2</sub> O <sub>4</sub>	Sr <sup>++</sup> × C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	5.6 × 10 <sup>-8</sup>
SrSO <sub>4</sub>	Sr <sup>++</sup> × SO <sub>4</sub> <sup>-</sup>	2.8 × 10 <sup>-7</sup>
SrCrO <sub>4</sub>	Sr <sup>++</sup> × CrO <sub>4</sub> <sup>-</sup>	? *
BaCO <sub>3</sub>	Ba <sup>++</sup> × CO <sub>3</sub> <sup>-</sup>	8.1 × 10 <sup>-9</sup>
BaC <sub>2</sub> O <sub>4</sub>	Ba <sup>++</sup> × C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	? *
BaSO <sub>4</sub>	Ba <sup>++</sup> × SO <sub>4</sub> <sup>-</sup>	1.1 × 10 <sup>-10</sup>
BaCrO <sub>4</sub>	Ba <sup>++</sup> × CrO <sub>4</sub> <sup>-</sup>	1.6 × 10 <sup>-10</sup>

\* Where the solubility product is in doubt on account of a questionable value for the solubility of the precipitate, a question mark (?) is used rather than omit the compound.

**Summary.**—A convenient method of expressing small decimal concentrations is to use decimal values of 10 to a negative power, as  $3.6 \times 10^{-4}$  for 0.00036.

An ion-product is the product of the ion concentrations from a solution of any degree of saturation, but the solubility product,  $K_{SP}$ , is the ion-product from a saturated solution, that is, it is the largest ion-product possible.

$K_{SP}$  is used only in connection with very dilute solutions, as from a sparingly soluble precipitate. The solution, although dilute, is saturated and therefore constant. It follows that  $K_{SP}$  is a constant and is derived from the relationships of a dilute but saturated solution. The value of  $K_{SP}$  is the reference value for precipitate formation.

### EXERCISES

1. Change the following decimal concentrations to the expressions involving the conventional negative powers of 10: 0.0<sub>3</sub>12, 0.0<sub>3</sub>6, 0.0<sub>7</sub>124, 0.0146.

2. Change the following to decimal values:  $8.4 \times 10^{-2}$ ,  $0.14 \times 10^{-4}$ ,  $0.53 \times 10^{-7}$ ,  $1.02 \times 10^{-14}$ .

3. Calculate the solubility products from the following concentrations of saturated solutions: AgBr,  $8.75 \times 10^{-7}$  moles per liter; CaCO<sub>3</sub>,  $3.05 \times 10^{-2}$  grams per liter; Mg(OH)<sub>2</sub>,  $1.2 \times 10^{-2}$  grams per liter.

## APPLICATIONS OF THE SOLUBILITY-PRODUCT PRINCIPLE

Mathematically, it is very easy to determine the ion concentration in a saturated solution from  $K_{SP}$ . Where  $[A^+][B^-] = K_{SP}$ , then  $[A^+]$  or  $[B^-] = \sqrt{K_{SP}}$ .

Using the  $K_{SP}$  for  $AgCl = 1.1 \times 10^{-10}$ :

$$[Ag^+] \text{ or } [Cl^-] = \sqrt{1.1 \times 10^{-10}} = \sqrt{1.1} \times \sqrt{10^{-10}} \\ = 1.05 \times 10^{-5} \text{ moles.}$$

Where the ionization is not taken to be 100 per cent, the  $K_{SP}$  can still be used to calculate the ion concentrations, but not the concentration of the saturated solution unless the per cent ionization is given. Suppose, in the last example, we assume that the  $AgCl$  is ionized only 98 per cent and that  $[Ag^+]$  and  $[Cl^-]$  are to be calculated from the previous value of  $K_{SP}$  which, of course, is only approximately correct for 98 per cent ionization:

$$\frac{98}{100} = \frac{1.05 \times 10^{-5}}{x},$$

or

$$x = \frac{105 \times 10^{-5}}{98}$$

*is 98% ionization*  
 $= 1.07 \times 10^{-5}m$ , the concentration of saturated  $AgCl$ .

It is evident that the molecular concentration cannot be calculated from  $K_{SP}$  unless the per cent ionization is given or a value assumed, because there would then be one equation with two unknown quantities. If the molecular concentration is to be calculated from  $K_{ion}$ , either the ion concentration or the per cent ionization must also be given, for the same reason.

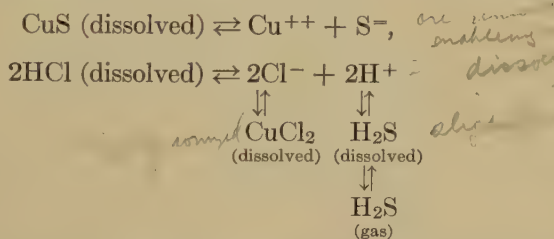
The solubility-product principle finds two very important applications in laboratory procedure, in the solution of precipitates, and in precipitating from solutions.

**The Solution of Precipitates.**—Where a precipitate is present, the entire system is said to be heterogeneous and not homogeneous,

because more than one phase <sup>3</sup> is present. The portion outside of the precipitate is homogeneous, however, and it is to this part of the mixture of solution and precipitate that the constants already considered apply.

It must also be remembered that:  $\text{AgCl (solid)} \rightleftharpoons \text{AgCl (dissolved but not ionized)}$ . Any change, therefore, in the conditions that decreases the concentration of  $[\text{Ag}^+]$  or  $[\text{Cl}^-]$  will make  $[\text{Ag}^+][\text{Cl}^-] < K_{\text{SP}}$ , and consequently more of the dissolved molecules will ionize to restore the equilibrium. In turn, more of the solid will dissolve to restore the equilibrium between solid and dissolved molecules. To have the solvent action continue, it is only necessary to keep  $[\text{Ag}^+][\text{Cl}^-]$  below  $K_{\text{SP}}$ . To do this, other molecules must be formed containing  $\text{Ag}^+$  or  $\text{Cl}^-$ , so that the resulting concentrations of  $\text{Ag}^+$  and  $\text{Cl}^-$  will give an ion-product that falls below that of  $K_{\text{SP}}$  for  $[\text{Ag}^+][\text{Cl}^-]$ .

Considering the solution of  $\text{CuS}$  in  $\text{HCl}$  and representing the double decomposition in the usual manner:



The salt  $\text{CuCl}_2$  is highly ionized and correspondingly removes very few  $\text{Cu}^{++}$  ions in undissociated molecules, but the  $\text{H}_2\text{S}$  is a very weak acid and so slightly ionized that a very large number of  $\text{S}^=$  ions are removed from the ionic equilibrium. The product  $[\text{Cu}^{++}][\text{S}^=]$  will, therefore, be kept less than the  $K_{\text{SP}}$  for  $\text{CuS}$  as

<sup>3</sup> A phase is one of the homogeneous portions of an inhomogeneous system; it has definite physical boundaries, and, furthermore, can be separated from other phases by physical means. Two phases do not have to be in two different *states of matter*, as mercury and water.

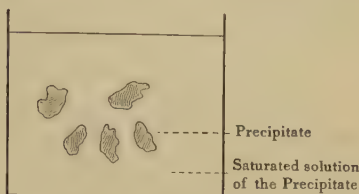
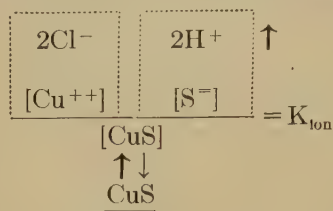


FIG. 3.—The Inhomogeneous or Heterogeneous System.

The entire system is inhomogeneous. The saturated solution is homogeneous and it is to this phase that the solubility-product principle directly applies.

long as the acid is in excess and  $\text{H}_2\text{S}$  is allowed to escape. The entire amount of  $\text{CuS}$  can in this manner be put into solution. Diagrammatically representing the entire process:<sup>4</sup>



Where precipitation is desired, the reverse process is involved. Instead of decreasing the concentration of one of the ions, the concentration is increased from some outside source. As soon as  $K_{\text{SP}}$  is exceeded, precipitation will begin and will continue so long as the common ion is added. As an example, let us consider a solution containing  $0.82 \times 10^{-5}$  moles of  $\text{AgCl}$  per liter. We have seen that a saturated solution is  $1.05 \times 10^{-5}m$ , so, of course, this solution is unsaturated. One method of starting precipitation would be to evaporate the solvent, thereby increasing the concentration to the point of precipitation. This, however, is not necessary, for, applying the  $K_{\text{SP}}$  principle where  $K_{\text{SP}} = [\text{Ag}^+][\text{Cl}^-]$  precipitation will begin just as soon as the product  $[\text{Ag}^+][\text{Cl}^-]$  exceeds  $1.1 \times 10^{-10}$ . Now  $[\text{Ag}^+]$  is limited by  $0.82 \times 10^{-5}$  moles, the amount of silver actually in solution. The concentration of  $[\text{Cl}^-]$  supplied by the  $\text{AgCl}$  is also  $0.82 \times 10^{-5}$  moles, but if we increase the  $[\text{Cl}^-]$  from some other source, as by adding  $\text{NaCl}$ , there will come a time when the  $[\text{Cl}^-]$  has been increased to such an extent that the product  $[\text{Ag}^+][\text{Cl}^-]$  will exceed the  $K_{\text{SP}}$  for  $\text{AgCl}$  and precipitation will begin. To determine how much  $[\text{Cl}^-]$  must be added to cause precipitation, substitute as follows:

$$1.1 \times 10^{-10} = [0.82 \times 10^{-5}][0.82 \times 10^{-5} + x],$$

where  $x$  = moles of  $\text{Cl}^-$  to be added.

Another substitution might be:

$$1.1 \times 10^{-10} = [0.82 \times 10^{-5}][x].$$

While in the first equation  $x$  is the amount of  $[\text{Cl}^-]$  to be added, in the second it is the total  $[\text{Cl}^-]$  required for precipitation, from

<sup>4</sup> A convenient method for distinguishing between the concentration of the dissolved molecules and that of the solid is as follows:  $[\text{CuS}]$  and  $\text{CuS}$ .

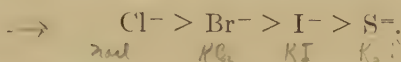


which the concentration present, namely  $0.82 \times 10^{-5}$ , must be subtracted to give the amount to be added. By either method,  $0.38 \times 10^{-5}$  of  $[\text{Cl}^-]$  is required.

A continued state of precipitation will require more and more  $\text{Cl}^-$  after  $K_{\text{SP}}$  has been originally exceeded.

By adding a large excess of  $\text{Cl}^-$  from some outside source, the  $\text{Ag}^+$  can be very nearly all precipitated. Beyond a certain point, however, further additions produce inappreciable results and, mathematically speaking, all of the  $[\text{Ag}^+]$  cannot be precipitated.

After adding a reasonable concentration of  $\text{Cl}^-$ , a more efficient method for a further precipitation of  $\text{Ag}^+$  would be to select ions whose solubility products with  $[\text{Ag}^+]$  are less than that for the chloride. Such a series of decreasing values will include the following:



*Important*

In qualitative analysis where the presence of a certain radical is to be determined by a precipitation method, it is evident that another radical must be added which will involve a  $K_{\text{SP}}$  less than the ion-product obtained, otherwise no test or precipitate will result. For this reason, where traces are to be determined, the reagent or conditions must be very different from those which involve a large amount of radical.

**Fractional precipitation** results when two or more radicals are present in solution and an oppositely charged radical is gradually added. The first precipitate that will form will be the one whose  $K_{\text{SP}}$  is the smallest. The separation of precipitates by this method is not as perfect as might be supposed, because of several complicated solution effects.

A second common-ion effect indirectly represses precipitation instead of promoting it. Suppose we are precipitating hydroxides with  $\text{NH}_4\text{OH}$ . To precipitate  $\text{Mg}(\text{OH})_2$  we must exceed  $K_{\text{SP}} = [\text{Mg}^{++}] [\text{OH}^-]^2$ . A saturated solution of  $\text{Mg}(\text{OH})_2$  is  $2.0 \times 10^{-4}m$ , and:

$$\begin{aligned} K_{\text{SP}} &= [2 \times 10^{-4}] [2(2 \times 10^{-4})]^2 \\ &= [2 \times 10^{-4}] [4 \times 10^{-4}]^2 \\ &= [2 \times 10^{-4}] [16 \times 10^{-8}] \\ &= 32 \times 10^{-12} \\ &= 3.2 \times 10^{-11}. \end{aligned}$$

If we add to a solution of  $\text{MgCl}_2$ , containing exactly  $2 \times 10^{-4}m$  of  $\text{Mg}^{++}$ , an equal volume of  $0.1m$   $\text{NH}_4\text{OH}$  having  $K_{\text{ion}} = 1.8 \times 10^{-5}$ , then the  $[\text{OH}^-] = \sqrt{1.8 \times 10^{-5}}$  or  $4.2 \times 10^{-3}$ . Finding the ion-product in this specific solution for  $[\text{Mg}^{++}] [\text{OH}^-]^2$  (not  $K_{\text{SP}}$  or the saturation value of the ion-product), we have:

$$[2 \times 10^{-4}] [2(4.2 \times 10^{-3})]^2 = 14.12 \times 10^{-9} \text{ or } 1.4 \times 10^{-8}.$$

Since  $1.4 \times 10^{-8}$  is larger than the value of  $K_{\text{SP}}$  or  $3.2 \times 10^{-11}$ , there will be a slight precipitation of  $\text{Mg}(\text{OH})_2$ .

The precipitation can, however, be prevented by first adding to the  $\text{MgCl}_2$  solution some  $\text{NH}_4\text{Cl}$  which will reduce or repress the  $[\text{OH}^-]$  as can be seen from:

Consisting of the  $\text{NH}_4^+$  from the  $\text{NH}_4\text{OH}$  and the  $\text{NH}_4\text{Cl}$

Reduced to a very small value

$$K_{\text{SP}} = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

The  $[\text{OH}^-]$  is now reduced to such a small value that the  $K_{\text{SP}}$  for  $\text{Mg}(\text{OH})_2$  will not be exceeded and no precipitate will be formed. It can thus be seen that the direct effect of the common ion is to promote precipitation, and the indirect effect to prevent it.

The effect of a common ion is very great where the other ion is polyvalent because the concentration is raised to some power in calculating  $K_{\text{SP}}$ . The difference can be seen by comparing:

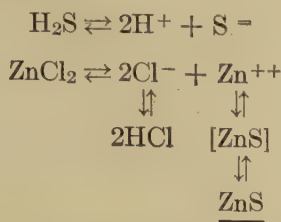
$$K_{\text{SP}(\text{NH}_4\text{OH})} = [\text{NH}_4^+] [\text{OH}^-],$$

$$K_{\text{SP}(\text{Ca}(\text{OH})_2)} = [\text{Ca}^{++}] [\text{OH}^-]^2.$$

In saturated solutions of each, the addition of the same  $[\text{OH}^-]$  will cause the formation of a greater number of associated molecules of  $\text{Ca}(\text{OH})_2$  than of  $\text{NH}_4\text{OH}$ .

In calculating the actual amount of precipitate that will form, instead of the simple fact that precipitation will take place, several factors must be considered, and the most important are (1) the concentrations of reacting substances, (2) the per cent ionization of each substance used and formed in the total volume of solution and (3) the solubility of the precipitate formed.

Where  $\text{ZnS}$  is precipitated from  $\text{ZnCl}_2$  by  $\text{H}_2\text{S}$ , we have:



When precipitation is complete there will remain, in a saturated solution of  $\text{ZnS}$ ,  $[\text{Zn}^{++}] = 3.5 \times 10^{-12}m$ , and the same concentration for  $[\text{S}^-]$ . The solubility product is  $(3.5 \times 10^{-12})^2 = 1.2 \times 10^{-23}$ . We can assume complete ionization for this very insoluble sulfide.

If we use one liter of  $0.1m$   $\text{ZnCl}_2$ , with an ionization in that concentration of 75 per cent, the concentration of zinc ions is  $0.075m$ . By adding  $0.1m$   $\text{H}_2\text{S}$ , which ionizes 0.05 per cent, there will be  $0.00005m$  of  $\text{S}^-$ . The product of the ion concentrations is then  $0.075 \times 0.00005 = 0.00000375$ , or  $3.75 \times 10^{-6}$ , which largely exceeds  $K_{\text{sp}}$ , and a precipitate will be formed. What actually happens is this: The  $\text{Zn}^{++}$  ions and  $\text{S}^-$  ions combine, forming associated molecules of  $\text{ZnS}$ , which, by increasing in number, finally saturate the solution, and then, as more ions combine, more associated molecules are formed; but, as the solution is now saturated, the excess comes out as a precipitate. For every  $\text{Zn}^{++}$  that combines with  $\text{S}^-$ , a molecule of  $\text{ZnS}$  is formed (but not necessarily precipitated), and if we let  $x$  equal the total molar concentration of  $\text{ZnS}$  formed by the reaction, we have:

$$(0.075 - x)(0.00005 - x) = 1.2 \times 10^{-23}.$$

Solving,  $x = 0.00005m$  (practically all of the  $\text{Zn}^{++}$ ).

The solution of the problem shows that when precipitation is taking place both ions combining to form the precipitate are removed at the same rate, and, if they were not originally present in equal concentrations, the one in less amount can be precipitated almost 100 per cent.

Where the precipitate has a much larger solubility, after solving for  $x$  as above, we must take into consideration the actual solubility of the precipitate and its ionization as well. Suppose the value of  $x$  is  $0.07m$  for  $\text{AD}$  formed, a saturated solution of  $\text{AD}$  is  $0.003m$ ,

and the ionization at this concentration is 96.3 per cent. Then the largest concentration of un-ionized molecules that can be present before precipitation starts equals

$$0.003m \times 0.037 = 0.000111m.$$

Finally,  $0.003 - 0.000111 = 0.002889$  mole, which will be the actual amount of precipitate settling out of the solution.

**Summary.**—Since  $K_{SP}$  is the product of the ion concentrations in a saturated solution, its value can be used to calculate the concentration of a saturated solution.

$K_{SP}$  applies to the saturated solution in contact with a precipitate.

By constantly decreasing the concentration of one or both ions present in a saturated solution in equilibrium with a precipitate, the solid can be dissolved. The ion concentration can be decreased by adding other ions that will form molecules less dissociated.

The common-ion effect consists in adding more of one of the ions represented in  $K_{SP}$ . When this is done the other factor in the product must correspondingly decrease in value. The common ion also promotes precipitation where a limited ion concentration is present, by giving the second factor such large values that  $K_{SP}$  is exceeded.

The amount of added ion necessary to begin precipitation can be calculated from  $K_{SP}$  relationships. The amount of precipitate can also be calculated.

### EXERCISES

1. Using values given in the table of solubility products, calculate the concentration of the metallic ion in saturated solutions of each of the following:  $PbSO_4$ ,  $MgCO_3$ ,  $BaCrO_4$ ,  $Zn(OH)_2$ .

2. If  $K_{SP}$  for  $BaSO_4$  is  $1.1 \times 10^{-10}$ , what is the normality of the saturated solution?

3.  $K_{SP}$  for water at  $18^\circ$  is  $0.59 \times 10^{-14}$ , and at  $100^\circ$  it is  $5.86 \times 10^{-13}$ . Calculate  $[H^+]$  at the two temperatures.

4. Select two precipitates and show by  $K_{SP}$  relationships how they can be dissolved by acids. What is the relative efficiency of a weak and a strong acid as a solvent?

5. Is the strength of an acid the only thing to be considered in dissolving a precipitate? (Lead sulfate, for example, is not soluble in sulfuric acid but does dissolve in ammonium acetate and acetic acid.)

6. To 50 cc. of a saturated solution of lead chromate are added 10 cc. of a 0.1*n* sodium chromate solution. How much precipitate will be formed? (Use the tables that have been given, and assume any other values which you may consider necessary.)

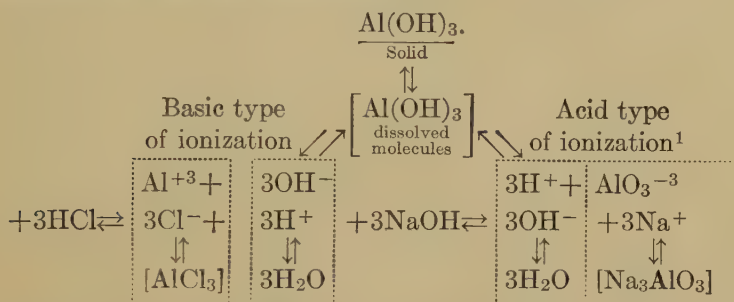


## CHAPTER VI

### AMPHOTERIC HYDROXIDES

**An amphoteric hydroxide** is one that ionizes both as an acid and as a base at the same time, or, in other words, furnishes  $H^+$  and  $OH^-$  in the same solution. This property is known as **amphoterism**. On account of this dual ionization, such an hydroxide should be able to react with either a base or an acid, forming a salt and water in either case.

We have seen in discussing the solution of precipitates that where a slightly ionized substance is formed in an equilibrium reaction the reaction will run practically to completion. Since water is only ionized to a small extent, an amphoteric hydroxide should be very soluble in either a strong acid or base. A graphical representation of the dual ionization and solution follows:



Both types of ionization can be represented by  $K_{\text{ion}}$  and, for  $\text{Al(OH)}_3$ , would have the following values:

$$K_{\text{ion as base}} = \frac{[\text{Al}^{+3}] [\text{OH}^-]^3}{[\text{Al(OH)}_3]};$$

$$K_{\text{ion as acid}} = \frac{[\text{H}^+]^3 [\text{AlO}_3^{-3}]}{[\text{Al(OH)}_3]}.$$

<sup>1</sup>  $\text{H}_3\text{AlO}_3$  to a certain extent loses  $\text{H}_2\text{O}$  as follows:  $\text{H}_3\text{AlO}_3 \rightleftharpoons \text{HAlO}_2 + \text{H}_2\text{O}$ . The original formula will be retained in equation writing.

TABLE VIII—THE PERIODIC SYSTEM<sup>1</sup>

Group 0	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
R ...	R <sub>2</sub> O ...	RO ...	R <sub>2</sub> O <sub>3</sub> ...	RO <sub>2</sub> RH <sub>4</sub>	R <sub>2</sub> O <sub>3</sub> RH <sub>3</sub>	RO <sub>3</sub> RH <sub>2</sub>	R <sub>2</sub> O <sub>7</sub> RH	RO <sub>4</sub>
He 2 4.00	Li 3 6.94	Be 4 9.1	B 5 10.9	C 6 12	N 7 14.01	O 8 16	F 9 19	
Ne 10 20.2	Na 11 23	Mg 12 24.32	Al 13 27.1	Si 14 28.3	P 15 31.04	S 16 32.06	Cl 17 35.46	
A 18 39.88	K 19 39.1	Ca 20 40.07	Sc 21 44.1	Ti 22 46.1	V 23 51	Cr 24 52	Mn 25 54.93	Fe 26 55.84
	Cu 29 63.57	Zn 30 65.37	Ga 31 69.9	Ge 32 72.5	As 33 74.96	Se 34 79.21	Br 35 79.92	Co 27 58.97 Ni 28 58.68
Kr 36 82.92	Rb 37 85.45	Sr 38 87.63	Y 39 88.7	Zr 40 90.6	Cb 41 93.1	Mo 42 96.0	Ma 43 —	Ru 44 101.7
	Ag 47 107.88	Cd 48 112.4	In 49 114.8	Sn 50 118.7	Sb 51 120.2	Te 52 127.5	I 53 126.92	Rh 45 102.9 Pd 46 106.7
Xe 54 130.2	Cs 55 132.81	Ba 56 137.37	*	Hf 72 179	Ta 73 181.5	W 74 184.0	Re 75 —	Os 76 190.9
	Au 79 197.2	Hg 80 200.6	Tl 81 204.0	Pb 82 207.2	Bi 83 208.0	Po 84 (210?)	— 85	Ir 77 193.1 Pt 78 195.2
Nt 86 222.4	— 87	Ra 88 226.0	Ac 89 (230?)	Th 90 232.4	UX <sub>2</sub> 91 (234?)	U 92 238.2		

\* Between Ba and Hf are fifteen rare earth elements with atomic numbers 57-71 inclusive, as follows: La 57, Ce 58, Pr 59, Nd 60, — 61, Sm 62, Eu 63, Gd 64, Tb 65, Dy 66, Ho 67, Er 68, Tm 69, Yb 70, Lu 71. These do not fit into the system satisfactorily.

<sup>1</sup> Taken from Chapin's "Second Year College Chemistry," John Wiley & Sons, Inc., New York, p. 98.

It must not be inferred that these two constants are equal, because that would imply that the hydroxide ionizes to the same extent both as an acid and as a base. With  $\text{Al}(\text{OH})_3$  the basic type is more pronounced than the acid. With other amphoteric hydroxides it may be just the reverse. It is also evident that the stronger the acid or base added to the precipitate of  $\text{Al}(\text{OH})_3$ , the more rapid and complete will be the solvent action. When the acid or base added furnishes ion concentrations not largely in excess of that from the ionization of  $\text{H}_2\text{O}$ , the solvent action is practically zero.

Amphoterism and also the degree of acidic or basic ionization can be related to the position of the element in **the periodic classification**.

In qualitative analysis we have to deal chiefly with the amphoteric characteristics of the hydroxides of aluminum, chromium, zinc, antimony and tin. These elements occupy a central position in the table. Pronounced amphoterism is not characteristic of the elements whose hydroxides form very strong bases or acids.  $\text{Cr}^{+6}$  as placed in the table would seem to be an exception because here it gives the strong acid  $\text{H}_2\text{CrO}_4$ . In qualitative analysis we shall speak of the amphoteric characteristics of chromium hydroxide but it will involve  $\text{Cr}^{+3}$  and not  $\text{Cr}^{+6}$ .

If chromium were placed in the table with  $\text{Cr}^{+3}$  it would fall in the group with  $\text{Al}^{+3}$ , and the classification, as far as amphoterism is concerned, would be more in harmony. One of the criticisms of the periodic classification is that it unduly emphasizes the atomic weights and one particular valence of the element, and disregards many other important chemical properties.

Where an element has more than one valence and the hydroxides are amphoteric, the higher valence type will have the acidic ionization increased. The question has been raised whether all hydroxides are not amphoteric to a certain degree, and there is some support for this assumption.

Differences in the acidic and basic types of ionization of amphoteric hydroxides will be made use of in systematical analysis in separating certain hydroxides from others. Clark<sup>2</sup> and a few others designate an amphoteric substance as an ampholyte.

**Summary.**—An amphoteric hydroxide is one that ionizes both as an acid and as a base. The values of  $K_{\text{acid}}$  and  $K_{\text{base}}$  are not

<sup>2</sup> Clark's, "The Determination of Hydrogen Ions."

the same for the same hydroxide but vary with the ampholyte used.

The  $K_{\text{acid}}$  is increased where the valence of the metal is raised; hence to make an amphoteric hydroxide more soluble in a base an oxidizing agent can be added.

Hydroxides are not necessarily bases. The term ampholyte is often applied to substances exhibiting the property of amphoterism.

Amphoterism is made use of in qualitative separations.

### EXERCISES

1. What is meant by the statement: Amphoterism is a periodic function of the atomic weight?

2. Ferric hydroxide is not amphoteric; but if a compound of the formula  $\text{Na}_2\text{FeO}_4$  can be prepared, what is the valence of iron in this substance and the possibility of the corresponding hydroxide being amphoteric?

3. How would you test the amphoterism of the precipitate  $\text{AgOH}$ ?

4.  $\text{Al}(\text{OH})_3$  and  $\text{Cr}(\text{OH})_3$  are both precipitates, and the first dissolves in a solution of  $\text{NaOH}$  more readily than the second. What is shown concerning the values of  $K_{\text{acid}}$  and  $K_{\text{base}}$  of the two substances?

5. If an acid is slowly added to a solution of  $\text{Na}_3\text{AlO}_3$ , a precipitate of  $\text{Al}(\text{OH})_3$  will eventually form. Explain.

6. Can the addition of acid in Exercise 5 go on indefinitely in order to obtain more precipitate?

7. Sometimes a solution of  $\text{NH}_4\text{Cl}$  is added to  $\text{Na}_3\text{AlO}_3$  to cause precipitation. Explain.

8. If the formula of sodium chromate is  $\text{Na}_2\text{CrO}_4$ , what has taken place in the solution of  $\text{Cr}(\text{OH})_3$  in  $\text{NaOH}$ ?

9. How would you determine whether chromic or aluminic acid is the stronger?

10. When acid is slowly added to a solution containing both  $\text{Na}_3\text{AlO}_3$  and  $\text{Na}_2\text{CrO}_4$  until it is about neutral, the  $\text{Al}(\text{OH})_3$  precipitates, but the  $\text{Cr}(\text{OH})_3$  does not. Explain.

11. When solid  $\text{Al}(\text{OH})_3$  is dissolved in either a strong acid or a base, show that the action is practically complete when the ion-product,  $[\text{H}^+][\text{OH}^-]$ , is equal to  $K_{\text{water}}$ .



## CHAPTER VII

### SALT HYDROLYSIS

Water is most commonly regarded as a solvent and, of course, as such is very important, but it also takes part in many types of chemical reactions. The formula for crystallized copper sulfate is  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  which implies that 5 molecules of water are held in chemical combination with each molecule of copper sulfate. This water is known as **water of hydration**. More recently a **solvate theory** has been proposed in which the solvents in general are supposed to enter into some sort of combination with many dissolved substances. We also know that metallic oxides as a class react with water, forming hydroxides, and, correspondingly, non-metallic oxides can give oxygen acids.

In **hydrolysis** we are principally concerned with the ions of water, and salt hydrolysis will then imply a reaction between a salt and  $\text{H}^+$  and  $\text{OH}^-$  from water. Suppose we consider the ionization of water as expressed by the  $K_{\text{ion}}$ . At  $20^\circ$  each liter of pure water contains a concentration of  $\text{H}^+$  and  $\text{OH}^-$  almost exactly equal to  $1 \times 10^{-7}m$ , so that:

$$K_{\text{ion}} = \frac{(1 \times 10^{-7})(1 \times 10^{-7})}{\left[ \begin{array}{c} \text{concentration of} \\ \text{dissolved water} \end{array} \right]} \cdot \cdot \cdot \cdot \cdot \quad (27)$$

In solving ionization constants for water, where water is the solvent as well as the thing ionized, it is not a simple matter to represent the concentration of the dissolved molecules, but we do know that the ionization is so extremely small that we may consider the denominator a constant.

Solving (27) we have:

$$K_{\text{ion}} \times \text{a constant} = (1 \times 10^{-7})^2$$

or

$$K_{\text{water}} = (1 \times 10^{-7})^2.$$

$K_{\text{water}}$  will hereafter be referred to as the ionization constant<sup>1</sup> for water, although it is really the solubility product for water and not the  $K_{\text{ion}}$  as previously used.

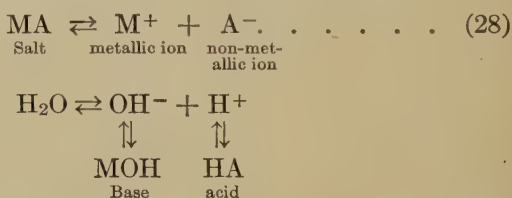
Since the ionization of water is increased quite rapidly by an increase in temperature, it is evident that to promote hydrolysis it is necessary to have plenty of water present as well as heat.

TABLE IX

THE EFFECT OF CHANGE OF TEMPERATURE UPON THE DISSOCIATION CONSTANT OF WATER

Temperature	$K_w$
0°	$0.12 \times 10^{-14}$
18°	$0.59 \times 10^{-14}$
25°	$1.04 \times 10^{-14}$
50°	$5.66 \times 10^{-14}$
100°	$58.20 \times 10^{-14}$

A general graphical representation of salt hydrolysis is:



It can be seen that in this reaction an acid and a base are formed, and the  $[\text{H}^+]$  and  $[\text{OH}^-]$  of the resulting solution will depend upon the relative strengths of the acid and base in question. Considering four possible types of salt hydrolysis:

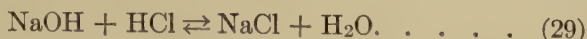
1. *MA*. Metal from a strong base, non-metal from a weak acid, as  $\text{Na}_2\text{CO}_3$ . In hydrolysis *MOH* will be a strong base and *HA* a weak acid, which will give a solution having an excess of  $\text{OH}^-$ , or the solution will give a basic reaction.

2. *MA*. Metal from a weak base and non-metal from a strong acid, as  $\text{CuSO}_4$ . The  $\text{H}^+$  will be in excess and the solution will give an acid reaction.

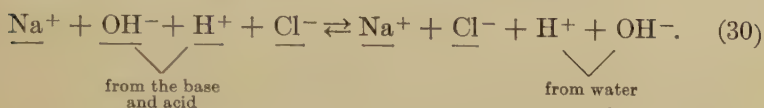
3. *MA*. Metal from a strong base and non-metal from a strong acid, as  $\text{NaCl}$ . The solution resulting from this possible hydrolysis is found to be neutral, and might be explained by

<sup>1</sup> Conventional or accepted usages are often not literally correct.

assuming that the strong base and strong acid formed are about equally ionized. The resulting solution would then contain the same concentrations of  $H^+$  and  $OH^-$ . Another explanation of the resulting neutral solution is that hydrolysis does not take place to any appreciable extent. In order to assist us in arriving at a conclusion let us examine the following equation in which a strong base is neutralized by a strong acid:



Since a reaction is largely one of ions, by rewriting and under-scoring the ions present in large quantities we have:



If the concentration of  $Na^+$  and  $Cl^-$  in both members is large and not far from equal, the equilibrium point will move to the right or left according to the concentrations of  $H^+$  and  $OH^-$ . These concentrations are so relatively small in the second member that the reverse reaction can be neglected, that is, the hydrolysis of  $NaCl$  is extremely small.

It is well to notice that neutralization and salt hydrolysis are the balanced parts of a certain equilibrium reaction. Salt hydrolysis is another reaction, the general character of which has been suggested to apply to all salts, and, although it has actually been determined that  $NaCl$  does hydrolyze to a very limited extent, this type of salt will be considered here to have no practical hydrolysis.

4. MA. Metal from a weak base and non-metal from a weak acid, as  $NH_4CN$ . If the acid and base have about equal strength, hydrolysis will not be indicated, just as in the case of type 3 by the excess of  $H^+$  or  $OH^-$ . By again referring to the equation in 3, it will follow that the  $[H^+]$  and  $[OH^-]$  are now comparable terms as derived from both sides of the equation and that hydrolysis takes place to a very large extent. Thus  $NH_4CN$  at room temperature is approximately 100 per cent hydrolyzed. Let it be restated that degree of hydrolysis is not indicated by acidity or alkalinity of the resulting solution alone.

The values of so-called **hydrolysis constants** can be mathematically represented by combining in various ways the three con-

stants  $K_w$ ,  $K_{\text{ion base}}$  and  $K_{\text{ion acid}}$ .<sup>2</sup> The most general relationship is:

$$K_{\text{hydrolysis}} = \frac{K_w}{K_{\text{acid}} \times K_{\text{base}}}. \quad \dots \quad (31)$$

The hydrolysis constant is, of course, a number, and it must be definitely understood what relationship between the three constants is indicated, otherwise no interpretation of the numerical value can be arrived at. In the general equation just given, the magnitude of hydrolysis can be noted by inspection. For example, since at a given temperature  $K_w$  has one value and  $K_{\text{acid}}$  and  $K_{\text{base}}$  depend upon the strength of acid or base involved, the amount of hydrolysis will then vary with  $K_{\text{acid}}$  and  $K_{\text{base}}$ . In general terms, if  $K_{\text{acid}}$  and  $K_{\text{base}}$  are large, since  $K_w$  is small, the value of the fraction will be very small, indicating little or no hydrolysis. However, if either factor of the denominator is small the fraction will have an increased value, and if both factors are small, as with a weak acid and base, the hydrolysis will be large. The hydrolysis constant so calculated will be in proportion to the degree of hydrolysis but will not be numerically equal to it.

In order to calculate the **per cent hydrolyzed**, we must use the fundamental equation:

$$\text{Per cent hydrolyzed} = \frac{\text{Amount of salt hydrolyzed}}{\text{Original or total amount of salt}} \times 100 \quad (32)$$

**In calculating the amount of salt hydrolyzed**, there are four facts that we shall use:

1. That the final concentration of the salt MA (the part not hydrolyzed), times its degree of ionization  $a_1$ , will give the value of  $[M^+]$  or  $[A^-]$ .

2. The concentration of the hydrolyzed part can be determined by finding the  $[H^+]$  or  $[OH^-]$  from the acid and base resulting from hydrolysis. (That is, for every molecule of the salt hydrolyzed there is also formed one molecule of acid and base.) We must remember that the actual  $[H^+]$  is equal to the total acid, HA, formed by hydrolysis, times  $a_2$ , its degree of ionization in the concentration present, and the actual  $[OH^-]$  is likewise equal to the base formed times  $a_3$ , its ionization.

<sup>2</sup>  $K_{\text{acid}}$  is the ionization constant of the acid from which the non-metal of the salt was derived.



3. That it is only necessary to work with either  $K_{\text{base}}$  or  $K_{\text{acid}}$ .

4. That  $K_w$  must also be used with whatever other constant is selected.

Suppose we work from the acid constant side. Then:

$$K_{\text{acid}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}, \quad \dots \quad (33)$$

and

$$K_w = [\text{H}^+][\text{OH}^-] \dots \quad (34)$$

Dividing (33) by (34):

$$\begin{aligned} \frac{K_{\text{acid}}}{K_w} &= \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \times \frac{1}{[\text{H}^+][\text{OH}^-]} \\ &= \frac{[\text{A}^-]}{[\text{HA}][\text{OH}^-]} \end{aligned}$$

Substituting our original statement (1) for the numerator and (2) for the denominator, we have:

$$\frac{K_{\text{acid}}}{K_w} = \frac{[\text{hydrolyzed MA}] a_1}{[\text{acid formed}] a_2 [\text{base formed}] a_3}, \quad \dots \quad (35)$$

and where there are  $x$  moles hydrolyzed,

$$\frac{K_{\text{acid}}}{K_w} = \frac{[\text{total MA} - x] a_1}{x^2 \cdot a_2 \cdot a_3} \dots \quad (36)$$

From which  $x$ , the moles of hydrolyzed salt, can be calculated. The per cent hydrolyzed is now a very simple matter, for it equals

$\frac{x}{\text{total AB}} \times 100$ . Note again that  $K_{\text{acid}}/K_w$  is a hydrolysis constant but not the degree of hydrolysis. This involves the calculation given in (32). The values for  $a_1$ ,  $a_2$  and  $a_3$  must be approximated because they depend, of course, upon the concentration of hydrolyzed salt, which we are determining. If the different values for the dissociation constants are disregarded, the last equation can very conveniently be rewritten:

$$\frac{K_{\text{acid}}}{K_w} = \frac{\text{total salt} - x}{x^2} \dots \quad (37)$$

Where one or more of the products of hydrolysis is a precipitate, the reaction will run very nearly to completion. This is true with

some of the sulfides which are precipitated in systematic analysis. The hydroxide may be more insoluble than the sulfide, and, although the sulfide may not be very soluble, yet the small part that is in solution is hydrolyzed, giving the more insoluble hydroxide. Where hydrolysis has been incomplete the product will naturally be a mixture.

A very convenient method for expressing acidity and alkalinity has been developed from the relationship,  $K_w = [H^+] [OH^-]$ . If the value at  $22^\circ$  is approximately  $1 \times 10^{-14}$ , it follows that  $[H^+]$  and  $[OH^-]$  are each equal to  $1 \times 10^{-7}$ . Suppose we now add a base, thereby increasing the value of  $[OH^-]$ . It follows that the concentration of  $[H^+]$  will be decreased since  $K_w$  remains unchanged. Similarly, the addition of an acid will increase  $[H^+]$  and decrease  $[OH^-]$ . Since the concentration of either an acidic or a basic solution can be expressed in terms of  $[H^+]$ , it follows that any system which will represent the concentration of hydrogen-ion without using the exceedingly small decimal values, such as,  $2.3 \times 10^{-7}$ , will be of great assistance.

The system commonly used to express hydrogen-ion concentration is based upon **pH units**. The meaning of the term pH can be derived as follows:

Where

$$K_w = [H^+] [OH^-] = 10^{-14},$$

$$[H^+] = 10^{-7} = \frac{1}{10^7}.$$

and

$$\frac{1}{[H^+]} = 10^7.$$

Then

$$\log \left[ \frac{1}{[H^+]} \right] = \log 10^7.$$

By definition we shall make  $\log \left[ \frac{1}{[H^+]} \right] = \text{pH}$ , and, since the log of  $10^7$  to the base 10 is 7, it follows that:

$$\text{pH of water at } 22^\circ = 7.$$

It is evident that where an acid is added to water the  $[H^+]$  will

increase; the value of  $\frac{1}{[H^+]}$  will decrease; and the corresponding log will decrease, that is, the  $pH$  values in acids will range from 7 downward, and those of bases from 7 upward. The following table will give the approximate  $pH$  values for several common acids and bases:

TABLE X

APPROXIMATE  $pH$  VALUES OF VARIOUS ACIDS AND BASES IN 0.1*n* SOLUTIONS AT 18°

Acids	$pH$ Value	Bases	$pH$ Value
Hydrochloric.....	1.0	Ammonia.....	11.3
Sulfuric.....	1.2	Sodium hydroxide.....	13.1
Phosphoric.....	1.5		
Acetic.....	2.9		
Carbonic.....	3.8		
Boric.....	5.2		

The  $pH$  values for various concentrations of HCl are given in the next table as they will be used in determining the acidity of Group II in metallic analysis.

TABLE XI

VALUES OF  $pH$  FOR SEVERAL CONCENTRATIONS OF HYDROCHLORIC ACID AT 18°

Normality of HCl	$[H^+]$	$pH$ Value
1.0	$8.0 \times 10^{-1}$	0.10
0.1	$8.4 \times 10^{-2}$	1.07
0.01	$9.5 \times 10^{-3}$	2.02
0.001	$9.7 \times 10^{-4}$	3.01
0.0001	$9.8 \times 10^{-5}$	4.01

**Summary.**—Because water ionizes, even though the extent is very limited, it can enter into reactions involving  $[H^+]$  and  $[OH^-]$ .

Salt hydrolysis is the reaction of a salt with the ions of water, giving a base and an acid.

Since the base and acid can be either weak or strong there are four possible types of hydrolysis. The strong-weak type gives



Research in the Norton Company, Worcester, Mass. Experiments made with the massive testing apparatus shown above are under the immediate control of the research laboratory shown below. The analyst is making an electrometric determination in which the end-point is determined electrically by means of a potentiometer.



upon hydrolysis a solution with  $[\text{OH}^-]$  in excess and reacts basic with an indicator; the weak-strong type gives an acid reaction; the strong-strong type is neutral and experiment shows hydrolysis to be negligible; the weak-weak type is neutral and the hydrolysis very complete.

Various  $K_{\text{hydrolysis}}$  are in use which are constants but do not represent the per cent hydrolysis. The amount of hydrolysis can be calculated from their values, and by comparing with the original concentration of salt, the per cent hydrolyzed can be found.

Many salts of weak acids are hydrolyzed after precipitation, and where the hydroxide is the less soluble compound it will be the final form of the precipitate.

A system for representing hydrogen-ion concentration involves the use of  $p\text{H}$  units.

### EXERCISES

1. Show how hydrolysis limits the completeness of neutralization.
2. Explain why hydrolysis becomes greater as  $K_{\text{base}}$  or  $K_{\text{acid}}$  approaches the value of  $K_w$ .
3. Borax gives an alkaline water solution. Explain.
4. Salts containing bivalent and trivalent metallic radicals are more readily hydrolyzed than those containing univalent metals. What conclusions can be drawn?
5. Will  $\text{NaHS}$  or  $\text{Na}_2\text{S}$  hydrolyze to the greater extent? (This is a good opportunity to decide whether the monobasic or dibasic acid is the stronger.)
6. Using data from your tables, calculate the per cent hydrolysis of a 0.1*n*  $\text{NH}_4\text{Cl}$  solution. Test a solution with litmus and see if, in general, your results agree.
7. Plot the values given in Table XI, using the vertical axis for normalities, and the horizontal axis for  $p\text{H}$  values. Save this curve for use in adjusting the acidity of Group II of metal analysis.

## CHAPTER VIII

### COMPLEX IONS AND AMMONIUM EQUILIBRIA

#### COMPLEX IONS

Before attempting to give a definition of a complex ion we shall consider some experimental data. If a  $0.01m$  solution of  $\text{NaOH}$  is slowly added to a  $0.1m$  solution of  $\text{AgNO}_3$ , a grayish-white precipitate of  $\text{AgOH}$  will be formed. This will quickly darken, owing to the formation of dark brown  $\text{Ag}_2\text{O}$ . Where more concentrated solutions are used the dark deposit will instantly result. An excess of  $\text{NaOH}$  produces no further change with the exception that the precipitate is diluted but not redissolved.<sup>1</sup>

This clearly proves that  $\text{AgOH}$  is not amphoteric, otherwise it would have dissolved in an excess of strong base. Again starting with  $0.1m$   $\text{AgNO}_3$ , we shall now add slowly  $0.1m$   $\text{NH}_4\text{OH}$ . As before, a grayish-white precipitate is formed which quickly darkens. If more  $\text{NH}_4\text{OH}$  is slowly added the density of the color begins to lighten and finally the precipitate completely dissolves. Two equivalents of  $\text{NH}_4\text{OH}$  are required to precipitate and completely redissolve one equivalent of  $\text{AgNO}_3$ , and the new molecule formed is  $\text{Ag}(\text{NH}_3)_2\text{OH}$ , silver-ammonia<sup>2</sup> nitrate.

<sup>1</sup> Misleading results are often obtained where an excess of reagent is diluting the precipitate and not really dissolving it. A good method of deciding the question is to allow the precipitate to settle in a test tube, pour off the liquid portion, and permit a very small amount of the precipitate to remain in the rounded portion of the tube. Now, by adding about 2 cc. of concentrated reagent, the excess will be so large that if its solvent action is of any reasonable value, solution should be practically complete. A turbidity resulting would indicate an inappreciable solvent action.

<sup>2</sup> Silver-ammonia and not silver-ammonium is used because it emphasizes the composition while passing over the possible ammonium structure. It is felt that the structure of ammonium compounds can be reserved to a later period if the presence of  $\text{NH}_3$  and not  $\text{NH}_4^+$  can be fixed in connection with ammonia complex ions.

The ionization of silver-ammonia nitrate is now graphically shown:

$$K_{\text{ion for the entire molecule}} = \frac{[\text{Ag}(\text{NH}_3)_2]^+ [\text{NO}_3]^-}{[\text{Ag}(\text{NH}_3)_2\text{NO}_3]} \quad \dots \quad (38)$$

The  $\text{Ag}(\text{NH}_3)_2^+$  further breaks up as shown by:

$$K_{\text{ion for } [\text{Ag}(\text{NH}_3)_2]^+} = \frac{[\text{Ag}^+] [\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2]^+} \quad \dots \quad (39)$$

We see from these two constants that the positive radical of the molecule is made up of  $\text{Ag}^+$  and  $\text{NH}_3^\circ$ , and in reactions the two move together and act as one ion having a univalent charge. The properties of  $\text{Ag}^+$  and  $\text{NH}_3^\circ$  are to a greater or less extent suppressed in the new combination and new properties have been developed just as  $\text{SO}_4^{=}$  is not like  $\text{S}^{=}$  and  $\text{O}^{=}$ . This type of radical is known as a **complex radical** and occupies an intermediate position between those of the type of  $\text{SO}_4^{=}$  and double salts like  $\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ , more commonly written,  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . In double salts we have, as the name implies, two salts which are held together in such a manner that the components have not lost their individual properties. Common alum, just used as an example, in solution gives the characteristic reactions for  $\text{K}^+$ ,  $\text{Al}^{+3}$  and  $\text{SO}_4^{=}$ .

The formation of complex radicals is not limited to a positive radical but may involve the negative as well, as in the following:  $\text{K}[\text{Ag}(\text{CN})_2]$ , potassium argenticyanide;  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , potassium ferri-cyanide. The weaker metal is in the non-metallic radical, and the same metal can be in both the metallic radical and the non-metallic complex as shown in the following reaction:



$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  is ferric ferrocyanide in which  $\text{Fe}^{++}$  is within the complex radical and  $\text{Fe}^{+3}$  is without. Complex-ion formation is limited to the heavier metals and frequently involves other valences than the ordinary or saturated type. (Look up secondary and free valence in any theoretical chemistry.) The formulas of molecules containing complex radicals cannot be completed by using unit valences. Sub-valences, or holding powers of extremely small values, are involved in complex-radical formation.

It must not be assumed that all molecules containing complex radicals are very soluble, because  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  is quite insoluble in neutral solutions or those of small acidity. The solubilities must be determined as for all molecules.

Complex ions may also have characteristic color values. The complex  $\text{Cu}(\text{NH}_3)_4^{++}$  is a deep blue, quite in contrast with the greenish blue of  $\text{Cu}^{++}$ . (See Plate I, *G* and *J*.)

The ionization constant for a complex ion is also known as the **complex constant** or the **instability constant**, and the equilibrium reactions involving complexes follow the same general plan as presented in other sections. The reprecipitation of a metal from a complex is of importance in analytical work and the process can be followed by again considering the silver-ammonia complex:

$$K_{\text{ion}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2]^+}$$

The value for this constant at  $25^\circ$ , resulting from a  $0.05m$  solution of  $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$ , is approximately  $6.8 \times 10^{-8}$ , and represents actual  $[\text{Ag}^+]$  equal to  $9 \times 10^{-4}m$ . In a  $0.1m$   $\text{AgCl}$  solution it has previously been found that  $[\text{Ag}^+]$  and  $[\text{Cl}^-] = 1.05 \times 10^{-5}m$ , so that by mixing equal volumes of the silver-ammonia nitrate solution and  $0.1m$   $\text{NaCl}$ ,<sup>3</sup>  $[9 \times 10^{-4}][8.5 \times 10^{-2}]$  will exceed  $[1.05 \times 10^{-5}]^2$ , the  $K_{\text{sp}}$  for  $\text{AgCl}$ , and a precipitate will be formed, that is, a positive test for  $\text{Ag}^+$  will result. The same amount of a bromide or iodide solution will, of course, give better results.

By adding an excess of  $\text{NH}_3$  (from  $\text{NH}_4\text{OH}$ ) to a solution of silver-ammonia nitrate, the  $[\text{Ag}^+]$  will be reduced by the common-ion effect so that the  $\text{NaCl}$  solution added in our previous experiment will no longer give a precipitate of  $\text{AgCl}$ . Conversely, if the  $[\text{NH}_3]$  is decreased, the  $[\text{Ag}^+]$  will be increased. This can be done by adding  $\text{HNO}_3$ , which will neutralize  $\text{NH}_4\text{OH}$  and in turn decrease the amount of  $\text{NH}_3$ . The  $[\text{Ag}^+]$  thus increased can finally precipitate as  $\text{AgCl}$  even though the amount of  $\text{Cl}^-$  is exceedingly small.

The solution of a precipitate by the formation of a complex is due, as in other types of precipitate solution, to the formation of a

<sup>3</sup>  $0.1m$   $\text{NaCl}$  ionizes about 85 per cent so that  $[\text{Cl}^-] = 0.1 \times 0.85 = 0.085 = 8.5 \times 10^{-2}m$ .



substance which ionizes to a smaller extent than the precipitate itself. The solution of AgCN in KCN will serve as an example:

$$K_{\text{ion AgCN}} = \frac{\boxed{\begin{array}{c} + \text{KCN} \\ [\text{Ag}^+] [\text{CN}^-] \end{array}}}{[\text{AgCN}]}$$

The complex  $\text{K}[\text{Ag}(\text{CN})_2]$  is formed. This has an ionization constant less than that for AgCN. The concentration of the ions in the numerator will therefore be decreased as KCN is added to the precipitate of AgCN, and to restore the equilibrium more AgCN will dissolve. It is interesting to note that if a complex were not formed there would be a common-ion effect and the solution of AgCN would be decreased. Another way to view the same situation is to conclude that when a common ion is added and solution results, a complex must have been formed.

**Summary.**—Complex ions consist of radicals in which the properties of the units have not been entirely suppressed, that is, the radical is in equilibrium with its dissociation products.

A complex ion may be considered to be the non-metallic part of a complex acid or the metallic part of a complex base.

The instability or degree of ionization is represented by the instability constant,  $K_{\text{instability}}$ , and is sometimes spoken of as the complex constant.

Some molecules containing complex ions are very soluble and others are very insoluble.

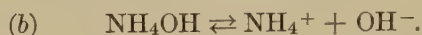
The formation of complex ions can be used in dissolving certain precipitates.

### EXERCISES

1. The salt CuCl is very insoluble in cold water but readily dissolves in  $\text{NH}_4\text{OH}$ . Explain.
2. What must be the relative values of  $K_{\text{SP}}$  of CuCl and  $K_{\text{inst.}}$  of the product formed in (1) to make solution possible?
3. CuS will not dissolve in  $\text{NH}_4\text{OH}$ . Explain.
4. Outline an experiment in which you could determine the formula of the complex produced by the solution of AgCN in KCN.
5.  $\text{Cu}(\text{NH}_3)_4^{++}$  and  $\text{Cd}(\text{NH}_3)_4^{++}$  will both give sulfide precipitates of the metals when  $\text{H}_2\text{S}$  is run into the solutions. Explain.
6. If KCN is added in excess to the solutions in Exercise 5 and then  $\text{H}_2\text{S}$  passed through, CdS alone will be precipitated. Why?

## AMMONIUM EQUILIBRIA

Reactions involving  $\text{NH}_4^+$  are more complicated than the simple reversible reactions on account of the fact that two reversible reactions are inter-related:



Since a solution of ammonia, as it is designated, is used as a convenient source of  $\text{NH}_4^+$ , it follows that we are using a solution containing a large amount of  $\text{NH}_3^\circ$  physically dissolved in water,<sup>4</sup> as well as a physical solution of  $\text{NH}_4\text{OH}$  molecules, which in turn ionize to furnish  $\text{NH}_4^+$  and  $\text{OH}^-$ . Any variation of  $[\text{NH}_4^+]$  or  $[\text{OH}^-]$  will, therefore, disturb two reversible reactions, the effect of which will ultimately be passed on to the  $\text{NH}_3$  dissolved. Although  $\text{NH}_4\text{OH}$  is a weak base and the actual  $[\text{NH}_4^+]$  or  $[\text{OH}^-]$  is small, the potential amount held in solution is quite large. The following equations will bring out the relationships:

From  $[\text{NH}_4\text{OH}] \rightleftharpoons [\text{NH}_3] + [\text{H}_2\text{O}]$ ,

$$K_{\text{eq}} = \frac{[\text{NH}_3][\text{H}_2\text{O}]}{[\text{NH}_4\text{OH}]}, \quad \dots \dots (41)$$

or

$$\frac{K_{\text{eq}}}{[\text{H}_2\text{O}]} = \frac{[\text{NH}_3]}{[\text{NH}_4\text{OH}]}. \quad \dots \dots (42)$$

But  $[\text{H}_2\text{O}]$  is a constant, so substituting  $K_1$  for  $K_{\text{eq}}/[\text{H}_2\text{O}]$ ,

$$K_1 = \frac{[\text{NH}_3]}{[\text{NH}_4\text{OH}]}. \quad \dots \dots (43)$$

Adding unity to both members,

$$K_1 + 1 = \frac{[\text{NH}_3]}{[\text{NH}_4\text{OH}]} + 1, \quad \dots \dots (44)$$

whence,

$$K_2 = \frac{[\text{NH}_3] + [\text{NH}_4\text{OH}]}{[\text{NH}_4\text{OH}]}, \quad \dots \dots (45)$$

<sup>4</sup> At  $0^\circ$ , 1300 volumes of gaseous  $\text{NH}_3$  will dissolve in 1 volume of water. Concentrated ammonia contains 35 per cent by weight of the gas.

and,

$$[\text{NH}_4\text{OH}] = \frac{[\text{NH}_3] + [\text{NH}_4\text{OH}]}{K_2} \quad \dots \quad (46)$$

But,



$$K_{\text{base, NH}_4\text{OH}} = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \dots \quad (47)$$

Substituting (46) in (47),

$$K_{\text{base}} = \frac{[\text{NH}_4^+] [\text{OH}^-]}{\frac{[\text{NH}_3] + [\text{NH}_4\text{OH}]}{K_2}}, \quad \dots \quad (48)$$

$$= \frac{K_2 [\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3] + [\text{NH}_4\text{OH}]}, \quad \dots \quad (49)$$

and

$$\frac{K_{\text{base}}}{K_2} = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_4\text{OH}] + [\text{NH}_3]}, \quad \dots \quad (50)$$

or

$$\underset{\text{A constant combining both reactions.}}{K} = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_4\text{OH}] + [\text{NH}_3]} \quad \dots \quad (51)$$

The last constant relates the  $[\text{OH}^-]$  to the entire source of  $\text{OH}^-$ , that is, the dissolved but un-ionized  $\text{NH}_4\text{OH}$  and the dissolved  $\text{NH}_3$ . The value of this constant has been found to equal  $1.8 \times 10^{-5}$  at  $18^\circ$ , and expresses the efficiency of ammonium hydroxide as a base. The ratio  $[\text{NH}_3]/[\text{NH}_4\text{OH}]$  is about 2, and the constant<sup>5</sup> for the ionization of dissolved  $\text{NH}_4\text{OH}$  into  $\text{NH}_4^+$  and  $\text{OH}^-$  is  $5 \times 10^{-5}$ . The efficiency constant for ammonia is generally the one given in tables.

<sup>5</sup> Moore, Jour. Chem. Soc., **91**, 1379 (1907).

## CHAPTER IX

### OXIDATION AND REDUCTION

In analytical chemistry there are numerous occasions where the valence of an element is changed in order to develop certain physical or chemical characteristics and thereby assist in ion separations and identifications. This process was referred to in the study of amphoterism. All valence changes, or, more correctly stated, all active valence changes involve a dual type of reaction, commonly known as an **oxidation-reduction reaction**.

**Oxidation** is concerned with the increase in the non-metallic portion of any compound, and since the amount of negative material is governed by the holding capacity of the positive radical, it follows that oxidation is also the increase in positive valence of the metallic portion. **Reduction** is, then, the reverse process. The radical  $O^-$  is negative and, where it is increased in amount in a compound, oxidation takes place. But any negative radical can be used and the process is the same, hence it follows that  $Fe^{++}Cl_2^-$  changed to  $Fe^{+3}Cl_3^-$  is just as much an oxidation process as where  $Fe^0$  (the metal) is converted into  $Fe_2^{+3}O_3^-$ .

The ionization of a substance from the free state can be either oxidation or reduction, depending upon whether a positive or a negative ion results. For example,  $Zn^0 \rightarrow Zn^{++}$  is oxidation, while  $Cl_2^0 \rightarrow 2Cl^-$  would be reduction. Algebraically, changing 0 to  $-$  is just as much a decrease in positivity as a change from  $+3$  to  $+2$  or from 1 to 0. This leads to a further consideration, namely, that if oxidation of a radical is an increase in its positivity, this can be accomplished by an increase in the negative content of the molecule, a decrease in the positive content or a corresponding change in both parts.

In accordance with modern theory,<sup>1</sup> all changes in valence are brought about by a movement of electrons, to or from the atom or

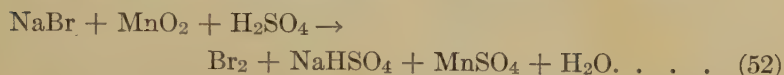
<sup>1</sup> See Chapin, Second Year College Chemistry, Chapter XI, John Wiley & Sons, Inc., New York, 1925.

ion. The positive nucleus remains a constant. Valence is, therefore measured in terms of this electronic change, and the basic definition would be:

**Oxidation is the removal of electrons from a body.** The statement in this form applies to a neutral atom as well as to one that is positive or negative. Conversely, **reduction is the addition of electrons.**

The dual nature of oxidation-reduction becomes very evident when we remember that, in order to remove electrons, something must remove them by adding them to its own structure. **A good oxidizing agent must therefore be readily reduced.**

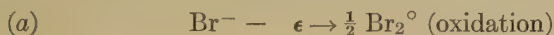
In balancing equations for oxidation-reduction reactions, the principles involved are the same as for all equation writing, with the exception that there must also be a balance in the valence changes or in the transfer of electrons. For example, suppose we bring into reaction  $\text{NaBr}$ ,  $\text{MnO}_2$ , and  $\text{H}_2\text{SO}_4$ . The first thing is to find out what the products are. This information must be determined experimentally.<sup>2</sup> In this reaction there are formed  $\text{Br}_2$ ,  $\text{NaHSO}_4$ ,  $\text{MnSO}_4$  and  $\text{H}_2\text{O}$ . Writing a trial equation:



We next examine the molecules in both members to determine any changes in valence, with the following result:

First Member		Second Member
$\text{Br}^-$	changes to	$\text{Br}_2^\circ$
$\text{Mn}^{+4}$	changes to	$\text{Mn}^{++}$

The electron interchange necessary to bring about these valence changes, where an electron is represented by  $\epsilon$ , will be:



or



In the first member in (a)  $2\epsilon$  are given out, and in (b)  $2\epsilon$  are added so that this member is in electron balance.

<sup>2</sup> Mathematical balances can only be used after the chemical facts are known. Compounds do not result which correspond to all possible mathematical subdivisions of formulas.

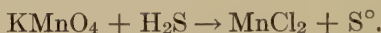


The second member contains  $\text{Br}_2^\circ$  which results from  $2\text{Br}^-$  losing  $2\epsilon$ , and  $\text{Mn}^{++}$ , the product of  $\text{Mn}^{+4}$ , gaining  $2\epsilon$ .

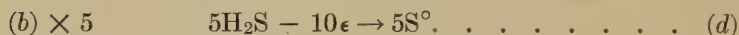
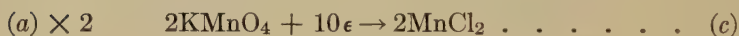
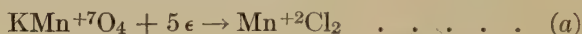
Where the same reaction is considered from the valence change viewpoint, we see that the loss of negative and positive valences has been the same. The completed equation then is:



Very often, in an oxidation-reduction reaction, only the ions having valence changes are written in the equation. As an example, consider the oxidation of  $\text{H}_2\text{S}$  by an acid permanganate solution, where the trial equation is:



Considering the valence and electron changes:

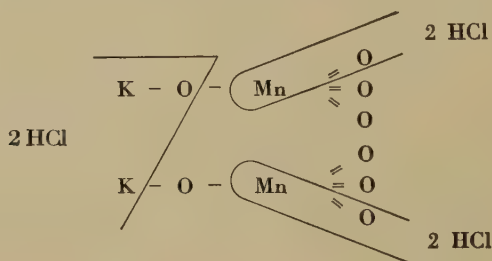


The final equation obtained from  $(a) + (b)$  is:



It is here assumed that there is an excess of acid. The oxidation ratio of 2 : 5 for  $\text{KMnO}_4 : \text{H}_2\text{S}$  gives the data necessary for quickly calculating various weights of  $\text{H}_2\text{S}$  oxidized by  $\text{KMnO}_4$  in an acid solution, that is, for every 2 molecules of  $\text{KMnO}_4$  used, 5 molecules of  $\text{H}_2\text{S}$  can be oxidized.

It is very helpful in many oxidation-reduction reactions to use **structural formulas** to visualize what is taking place. For example, using the  $\text{KMnO}_4$  of the last reaction:

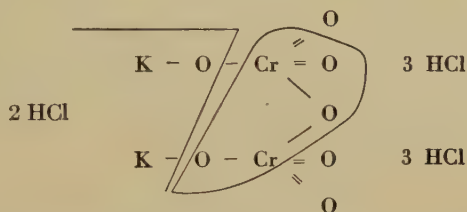


The permanganate acts in an acid solution as an oxidizing agent, because in the presence of the acid (HCl used here)  $K_2O$  and  $2MnO$  are removed, forming  $2KCl$ ,  $2MnCl_2$  and  $3H_2O$ . There is required  $6HCl$ , and 5 of  $O^-$  are, therefore, available for oxidation purposes. The substance to be oxidized is  $H_2S$  and the equation in this oxidation is:



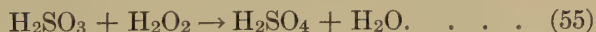
Since  $2KMnO_4$  furnish 5 of  $O^-$ , we have seen that the oxidation ratio is 2 of  $KMnO_4$  to 5 of  $H_2S$ . The electron interchange between the molecules is so simple that no equation is really necessary.

The decomposition of potassium dichromate in an acid solution is here shown:



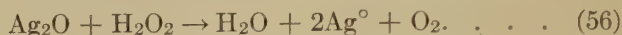
$Cr_2O_3$  dissolves in the acid and 3 of  $O^-$  are available from each molecule of the dichromate used. The electron interchange and oxidation ratio can be seen by inspection.

A few oxidation agents require special analysis. One of these is  $H_2O_2$ , which can act either as an oxidizing or as a reducing agent according to conditions. The structural formula is at present assumed to be  $H^+ - O^+ - O^- - H^+$ , in which one oxygen atom is polarized, that is, shows one negative valence toward a hydrogen atom and a plus valence toward an oxygen atom. In a weakly acid solution the peroxide reacts as an oxidizing agent by adding  $2\epsilon$  to each of its molecules and changing the  $-O^+$  to  $-O^-$  with  $H_2O$ , the other product of its decomposition. The  $O^-$  now combines with the molecule that is to be oxidized as:



As a reducing agent there must be present, with the peroxide, a strong oxidizing agent as  $Ag_2O$  or  $PbO_2$ . Under these conditions the  $-O^+$  of the peroxide loses  $2\epsilon$ , becoming  $+O^+$  which together

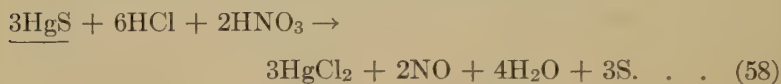
with the  $-O^-$  is eliminated as  $O_2$ . The structural formula of the neutral gas molecule is  $+O^+ - O^-$  or, as customarily represented,  $O_2^\circ$ . The substance reduced furnishes  $O=$  to combine with the residual  $2H^+$  of the peroxide to form water as represented by:



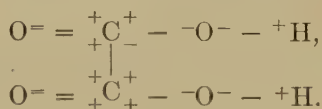
Aqua regia is a powerful oxidizing agent and is used as a solvent for some of the heavy metals and their sulfides. It is made up of 3 parts of concentrated  $HCl$  and 1 part of concentrated  $HNO_3$ . The interaction of these acids is shown by:



The equation shows the presence of three oxidizing agents,  $HNO_3$ ,  $Cl_2$  and  $NOCl$ . The  $NOCl$  may furnish  $HNO_2$  by hydrolysis with water. With this reagent the oxidation of  $S^\circ$  will not stop with  $S^\circ$  but will proceed to  $SO_4^{+6}$  where the valence of sulfur is  $S^{+6}$ . The solution of  $HgS$  in aqua regia is shown by:



Oxalic acid is a reducing agent and a study of its structural formula furnishes another example of atoms presenting two types of holding power to two adjacent and dissimilar atoms:



When oxalic acid is decomposed by the addition of  $H_2SO_4$  there results  $H_2O$ ,  $CO_2$ , and  $CO$ . When oxalic acid reduces,  $H_2O$  and  $CO_2$  are its end products. It is evident, then, that either one carbon in oxalic acid has a valence of 2 or that the carbon-carbon linkage is accomplished as shown in the diagram by a polarized  $- +$  combination. In either case,  $2\epsilon$  are given out when one molecule of oxalic acid is oxidized.

The **oxidizing valence** of a substance is the actual valence change available for oxidizing purposes and the **oxidizing equivalent weight** will involve the corresponding fraction of a formula weight.

Some of the more common types of oxidizing and reducing agents involving electronic changes are given in the following table:

TABLE XII

ELECTRON TRANSFER INVOLVED IN SOME OF THE COMMON OXIDIZING AND REDUCING SUBSTANCES

## OXIDIZING SUBSTANCES

Substance and Original Valence	Electrons Gained		Final Valence*
$O_2^0$	$+4e$	$\rightarrow$	$2O^{-2}$
$Cl_2^0$	$+2e$	$\rightarrow$	$2Cl^{-}$
$KCl^{+5}O_3$	$+6e$	$\rightarrow$	$Cl^{-}$
$HN^{+5}O_3$ (dil.) †	$+3e$	$\rightarrow$	$N^{+2}$
$HN^{+5}O_3$ (conc.)	$+e$	$\rightarrow$	$N^{+4}$
$KMn^{+7}O_4$ (in acid)	$+5e$	$\rightarrow$	$Mn^{+2}$
$KMn^{+7}O_4$ (in base)	$+3e$	$\rightarrow$	$Mn^{+4}$
$K_2Cr_2^{+6}O_7$ (in acid)	$+6e$	$\rightarrow$	$2Cr^{+3}$
$K_2Cr^{+6}O_4$ (in base)	$+3e$	$\rightarrow$	$Cr^{+3}$
$H_2O_2^{\ddagger}$	$+2e$	$\rightarrow$	$O^{-2}$
$Pb^{+4}O_2$	$+2e$	$\rightarrow$	$Pb^{+2}$

\* The final radical is given but the compound which is actually formed depends upon the reacting substances present.

† The oxidizing value of  $HNO_3$  depends upon the concentration, temperature and metal with which it reacts. A series of reduction products may result which involve different electron transfers.

‡ See preceding paragraphs for a discussion of valence change in  $H_2O_2$ .

## REDUCING SUBSTANCES

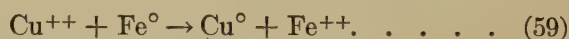
Substance and Original Valence	Electrons Lost		Final Valence
$H_2^0$	$-2e$	$\rightarrow$	$2H^{+}$
$Zn^0$	$-2e$	$\rightarrow$	$Zn^{+2}$
$H_2S^{+4}O_3$	$-2e$	$\rightarrow$	$H_2S^{+6}O_4$
$H_2S^{-2}$	$-2e$	$\rightarrow$	$S^0$
$S^0$	$-6e$	$\rightarrow$	$S^{+6}O_4$
$H_2C_2O_4^*$	$-2e$	$\rightarrow$	$C^{+4}O_2$
$Fe^{+2}SO_4$	$-e$	$\rightarrow$	$Fe^{+3}$
$Sn^{+2}Cl_2$	$-2e$	$\rightarrow$	$Sn^{+4}$
$2KI^{-}$	$-2e$	$\rightarrow$	$I_2^0$
$H_2O_2$	$-2e$	$\rightarrow$	$O_2^0$

\* See preceding paragraphs for discussions of valences of the carbon atoms in oxalic acid.

It must be emphasized that an oxidation-reduction pair cannot be selected at random from the two tables just presented. Substance A may take electrons from B, but when brought in contact with substance C it may lose electrons. It follows, then, that under suitable conditions an oxidizing substance may be further oxidized instead of being reduced. It is entirely possible to select two substances from the same oxidation or reduction table that will react as an oxidation-reduction couple.

To show how a radical can be made to react against its fundamental valence-change tendency, let us pass  $\text{H}_2\text{S}$  through a solution of  $\text{FeCl}_3$ . The tendency for the iron radical is to go from  $\text{Fe}^{++}$  to  $\text{Fe}^{+3}$ , that is, to give out electrons. But the tendency for the  $\text{S}^-$  of the  $\text{H}_2\text{S}$  is also to go from  $\text{S}^-$  to  $\text{S}^0$  with the elimination of electrons. When the two are brought together, it follows that both cannot lose electrons, and, since the  $\text{S}^-$  has the greater power of elimination, the electrons are forced upon the  $\text{FeCl}_3$ , which reduces it to  $\text{FeCl}_2$ . The ferric chloride, in other words, has been forced to assume the rôle of an oxidizing substance.

An interesting example of an oxidation-reduction pair selected from the same series consists in selecting two metals from a group generally referred to as the electromotive or electrochemical series. Metallic iron, for example, when placed in a solution of  $\text{CuSO}_4$  will become coated with copper, and iron will go into solution. The reaction is:



The  $\text{Fe}^0$  evidently loses  $2\epsilon$  and the  $\text{Cu}^{++}$  gains  $2\epsilon$ , or the iron is oxidized and the copper reduced. Frequently an analytical test can be made by displacing a metal from a solution. The following table gives the relative displacing or oxidizing powers of the metals:

TABLE XIII  
DISPLACEMENT SERIES OF THE METALS

A metal will displace another lower in the series in  $0.1m$  solutions; and the greater the difference in position, the more efficient will be the displacement.

Potassium	Manganese	Nickel	Arsenic
Sodium	Zinc	Tin	Copper
Barium	Chromium	Lead	Mercury
Calcium	Iron	Hydrogen	Silver
Magnesium	Cadmium	Antimony	Platinum
Aluminum	Cobalt	Bismuth	Gold



The tendency to give off or take up electrons can be measured in terms of a suitable pressure unit known as unit potential difference, or one volt. This is the basis of our next section.

**Summary.**—Oxidation is the increase of the non-metallic constituent of a compound. This involves the increase of positive valence of the metallic radical, which in turn is accomplished by the removal of electrons. Reduction is the reverse of the above. In terms of valence change, oxidation is the increase of + valence of a metallic radical or the decrease of - valence of a non-metallic radical.

The oxidation of one substance is accompanied by the simultaneous reduction of another.

Oxidation-reduction reactions can be balanced by the valence-change method or by the electron-transfer method.

The study of the structural formula is of great assistance in understanding oxidation-reduction reactions.

In numerical problems the oxidation or reduction ratio is of great importance.

Great care must be exercised in selecting pairs of oxidizing-reducing substances, or the reducing substance may turn out to be the one that does the oxidizing.

A displacement series of metals is based upon the relative oxidation-reduction tendency.

### EXERCISES

1. Indicate the valences of the atoms in the following molecules:  $\text{H}_3\text{PO}_4$ ,  $\text{KMnO}_4$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7$ ,  $\text{SnCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{H}_2\text{SO}_4$ .

2. Write structural formulas for the following and indicate all valences:  $\text{KClO}_3$ ,  $\text{CrO}_2\text{Cl}_2$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{NH}_4\text{OH}$ .

3. The following changes show the part of a reaction which involves a particular change of valence by oxidation or reduction. State which process is involved:  $\text{Br}_2 \rightarrow \text{AgBr}$ ,  $\text{HAsO}_3^- \rightarrow \text{AsH}_3$ ,  $\text{Pb}^{++} \rightarrow \text{PbO}_2$ ,  $\text{P} \rightarrow \text{H}_2\text{PO}_4^-$ ,  $\text{Cr}(\text{OH})_3 \rightarrow \text{CrO}_4^-$ ,  $\text{F}_2 \rightarrow \text{MnF}_6^{-3}$ ,  $\text{C}_2\text{O}_4^- \rightarrow \text{CO}_3^-$ ,  $\text{NO}_3^- \rightarrow \text{NO}_2$ ,  $\text{NH}_2\text{OH} \rightarrow \text{NH}_4^+$ .

4. Write completely balanced equations for the oxidation-reduction reactions involving the following: Mercuric chloride and stannous chloride; potassium dichromate and hydrosulfuric acid in an acid solution; oxalic acid and potassium permanganate; tin and nitric acid; potassium iodide and chlorine water; chromic hydroxide and sodium peroxide; zinc and silver nitrate.

### OXIDATION-REDUCTION REACTIONS RELATED TO ELECTRIC CURRENT

Modern theory considers an electric current to be a flow of electrons through a conductor. The conductor may be metallic or may be an electrolytic solution. If oxidation is the removal of electrons and reduction the addition of electrons, the question naturally arises whether the two processes cannot be accomplished

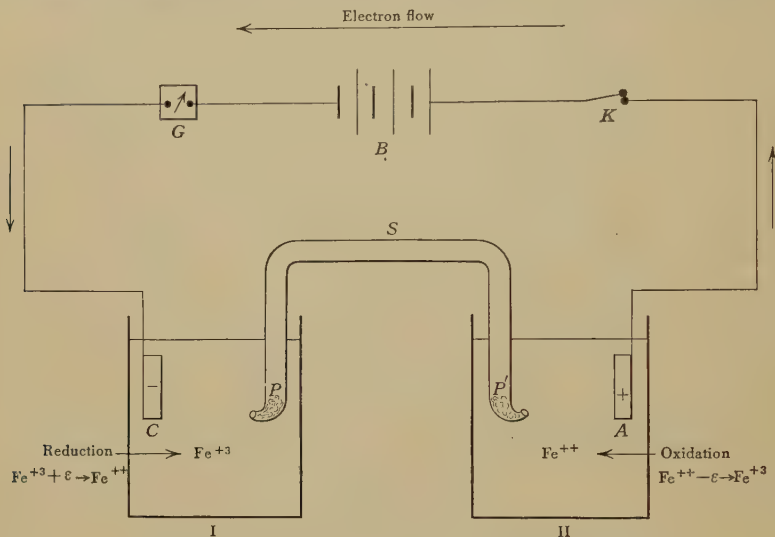


FIG. 4.—Oxidation-reduction by an Electric Current.

G, galvanometer; B, battery; K, key; A, anode; C, cathode; P, P', cotton plugs; S, salt bridge.

by electrical methods. The above diagram will show how this is actually possible.

The glass beaker I contains a solution of  $\text{FeCl}_3$ , and II, a solution of  $\text{FeCl}_2$ . A salt bridge, S, consists of a bent piece of glass tubing, containing a suitable salt solution, and is used as an electrolytic conductor between the beakers. The ends of the tubing are plugged with cotton to prevent excessive diffusion into the beakers. This does not prevent the electrical transfer of ions. C and A are two contact terminals, known as **electrodes**, and are made of platinum or some other substance that will not react with the solutions. They are designated as C, the **cathode**, which will carry

the electrons into beaker *I*, and *A*, the **anode**, by which the electrons leave the beaker *II*. The electron flow is shown by arrows and is determined experimentally by the needle displacement of the galvanometer, *G*. The battery, *B*, is the power source and supplies electrons to electrode *C* and removes them from *A*. The action in *I* is partially represented by  $\text{Fe}^{+3} + e \rightarrow \text{Fe}^{+2}$ , and in *II* by  $\text{Fe}^{+2} - e \rightarrow \text{Fe}^{+3}$ . In *I*, then, reduction is taking place about the negative terminal, and in *II* there is oxidation.

The oxidation-reduction reaction accomplished by an electric

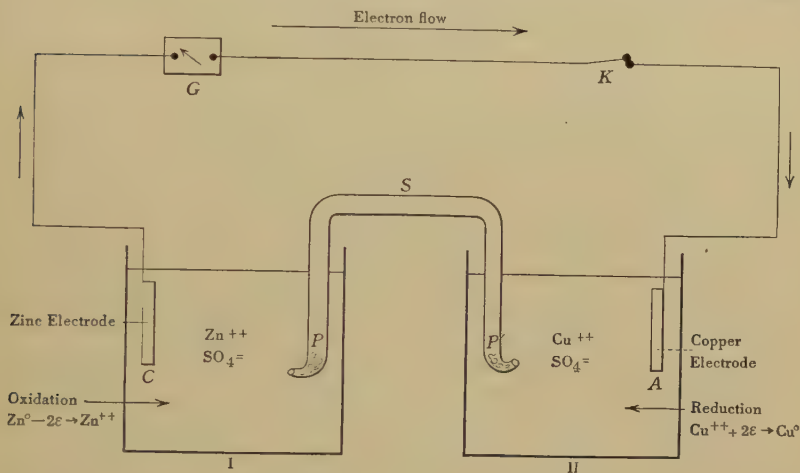


FIG. 5.—An Electric Current Produced by an Oxidation-reduction Reaction.

*G*, galvanometer; *K*, key; *A*, plus electrode of cell; *C*, negative electrode of cell; *P*, *P'*, cotton plugs; *S*, salt bridge.

current constitutes **electrolysis**, and many interesting experiments can be performed in oxidizing substances about the anode and reducing others about the cathode. For example, colorless  $2\text{I}^-$  changes to brown  $\text{I}_2^0$ , orange-red  $\text{Cr}_2\text{O}_7^{--}$  becomes green  $\text{Cr}^{+3}$ , dissolved metals are deposited, purple  $\text{MnO}_4^-$  changes to a colorless solution, and many other experiments immediately suggest themselves.

Where oxidation-reduction reactions produce an electric potential, the complete processes are a little more involved than with electrolysis but the basic principle is the same. The current-generating cell, or **primary cell**, consists of two parts, one of which

furnishes electrons by oxidation while the other takes in electrons by a reduction process.

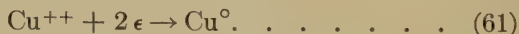
Using the same type of apparatus as before, we shall put in *I* some  $\text{ZnSO}_4$  in contact with a zinc electrode, and in *II*  $\text{CuSO}_4$  against a copper electrode. Copper has a greater tendency to take up electrons than it has to get rid of them, or where  $\text{Cu}^{++}$  is in solution the tendency will be to pass from  $\text{Cu}^{++}$  to  $\text{Cu}^\circ$ , which, of course, requires electrons. Zinc, on the other hand, has a greater tendency to change from  $\text{Zn}^\circ$  to  $\text{Zn}^{++}$ ; consequently, when in combination in a primary cell, the reaction will be:



and electrons will flow from *I* to *II* through the external conductor.

Notice especially that in changing from electrolysis to a primary cell with the + and - electrodes remaining in the same right- and left-hand positions, the oxidation and reduction sections have reversed as well as the current. This is as it should be because an action that produces a flow of current should certainly oppose a current in the direction that would tend to destroy that action.

Although oxidation takes place in *I*, the oxidizing substance should be considered to be in *II*, and, correspondingly the reducing substance is in *I*. This is in harmony with our assumption, because if  $\text{Cu}^{++}$  is the oxidizing substance it should be reduced and we have shown that reduction actually occurs in *II*, by:



The purpose of the salt bridge can be understood by considering that there will be a gradual increase of  $\text{Zn}^{++}$  in *I* and of  $\text{SO}_4^{=}$  in *II*, which in time would **polarize** the cell by creating a back action. The salt bridge allows a compensating action to proceed, and this compensating action, by the proper movement of ions through the bridge, relieves the polarizing tension.

The oxidation or reduction potential depends not only upon the electrode and the solution but also upon the concentration of solution used. The relationship will not, however, be developed further.<sup>3</sup>

<sup>3</sup> See Creighton and Fink, *Electrochemistry*, John Wiley & Sons, Inc., New York, Vol. I, Chapter X, 1928.

TABLE XIV

## OXIDATION-REDUCTION POTENTIALS

Either a metal in a normal concentration of the metal ion is used, or two normal solutions of the metal ion in two states of oxidation. The reference potential is that between  $H^{\circ}$  and  $n H^{+}$ , and is 0 in the table.

Oxidation-Reduction Pairs	Volts
$K^{\circ}-K^{+}$	+2.92
$Na^{\circ}-Na^{+}$	+2.71
$Mg^{\circ}-Mg^{++}$	+1.55
$Al^{\circ}-Al^{+3}$	+1.34
$Mn^{\circ}-Mn^{++}$	+1.00
$Mn^{+4}-Mn^{+3}$ in 15 <i>n</i> $H_2SO_4$	+1.60
$Zn^{\circ}-Zn^{++}$	+0.76
$Cr^{+3}-Cr^{++}$ in 0.1 <i>n</i> HCl	+0.40
$Fe^{\circ}-Fe^{++}$	+0.44
$Fe^{+3}-Fe^{++}$ in weak acid	+0.74
$Fe(CN)_6^{-3}-Fe(CN)_6^{-4}$	+0.41
$Cd^{\circ}-Cd^{++}$	+0.40
$Ni^{\circ}-Ni^{++}$	+0.20
$Sn^{\circ}-Sn^{++}$	+0.14
$Pb^{\circ}-Pb^{++}$	+0.12
$Fe^{\circ}-Fe^{+3}$	+0.05
$H_2^{\circ}-2H^{+}$	0.00
$Sn^{\circ}-Sn^{+4}$	-0.05
$Sn^{+4}-Sn^{++}$ in HCl	-0.41
$Sn^{+4}-Sn^{++}$ in NaOH	-0.85
$Cu^{\circ}-Cu^{++}$	-0.34
$Cu^{\circ}-Cu^{+}$	-0.52
$2Hg^{\circ}-Hg_2^{++}$	-0.80
$Ag^{\circ}-Ag^{+}$	-0.80
$Hg^{\circ}-Hg^{++}$	-0.86
$Au^{\circ}-Au^{+}$	-1.50

The order of the metals in the electromotive series is the same as above.

A primary cell develops a potential difference which is principally the difference between two potential differences. For example, the  $Zn^{\circ}/Zn^{++} - Cu^{++}/Cu^{\circ}$  combination previously described will furnish a potential difference between the electrodes of  $0.76 - (-0.34) = 1.10$  volts where the solution concentrations are normal. The algebraic difference of the potentials is taken because the two effects cause the electrons to move in the same direction, that is, they form a push-pull combination and the moving power is therefore equal to  $0.76 + 0.34$  volts.



**Summary.**—An electric current flowing through a solution of an electrolyte will oxidize the ions about the + electrode and reduce those about the - electrode.

Conversely, an electric current can be made to flow as a result of a chemical reaction by having an oxidation-reduction reaction take place in such a manner that it removes electrons from one terminal of a primary cell and supplies them to the other terminal.

The voltage of a cell can be calculated from electrode potentials.

An electrode potential is established between a substance in two states of oxidation and is specific for the combination used.

#### EXERCISES

1. In the  $\text{ZnSO}_4\text{-CuSO}_4$  cell a momentary flow of current is noticed when the external circuit is closed without the salt bridge in position, but this flow soon drops to zero. Explain.

2. Why is the current continuous when the salt bridge is in place?

3. When  $\text{NH}_4\text{OH}$  is added to the  $\text{CuSO}_4$  solution, there is a drop in current. Why?

4. Explain why there is a further drop when  $\text{KCN}$  is added to the same cell.

5. Show how the current can be increased. (Use several different substances and do not give all of your attention to just one of the cell divisions.)

## CHAPTER X

### DISTRIBUTION OF A SOLUTE BETWEEN TWO IMMISCIBLE SOLVENTS; COLLOIDAL SUSPENSIONS

#### DISTRIBUTION OF A SOLUTE BETWEEN TWO IMMISCIBLE SOLVENTS

In a few analytical tests, a solute which is dissolved in one solvent is extracted by shaking with another more effective solvent in order to concentrate this solute in the extracting solvent. Iodine is sparingly soluble in water but is very soluble in carbon bisulfide or chloroform. In order to determine if there is a small amount of dissolved iodine in an aqueous solution, a few drops of carbon bisulfide are added, and, after being thoroughly shaken, the liquids are allowed to settle. A pink color in the  $\text{CS}_2$  layer will indicate the higher concentration of the iodine in that solvent. The two solvents must not dissolve in each other to an appreciable extent, that is, they must be **immiscible**, and their solvent powers for the particular solute must be quite widely different.

Since the solvent action of each liquid is not determined by the presence of the other, their ratio can be expressed by a constant which is known as the **distribution-ratio constant**, or the **partition coefficient**. The relationship was developed by Nernst<sup>1</sup> and the mathematical equation is:

$$K_{\text{dist. coef.}} = \frac{C_A}{C_B}, \quad . . . . . (62)$$

where  $C_A$  is the concentration of the substance in solvent A, and  $C_B$  that in solvent B.

Better extraction will result when the more efficient solvent is used as the extracting agent, in portions rather than in one operation involving the entire volume. As an example we can take a certain solute that is twice as soluble in benzene as in water. If we have 1 gram of the solute in a certain volume of water it would

<sup>1</sup> Zeit. Phys. Chem., 8, 110 (1891).

require 2 grams to saturate the same volume of benzene. If we start with the water solution and add the entire volume of benzene in one extracting operation, there will be 1 gram of solute distributed between two volumes of mixed solvents. Where  $x$  grams are removed by the benzene,  $1 - x$  grams will remain in the water. But, by the conditions of the problem,  $x$  is twice as large as  $1 - x$ , and to form an equation  $x$  must be divided by 2, or  $(1 - x)$  multiplied by 2. Then:

$$\begin{aligned}x &= 2(1 - x), \\x &= 2 - 2x, \\3x &= 2;\end{aligned}$$

$x = \frac{2}{3}$  gram or 67 per cent.

A very common error is to state that one-half is extracted by the benzene. The problem, arithmetically expressed, is to divide 1 gram into two parts, one of which shall be twice as large as the other.

Suppose we now start as before but add only one-half of the volume of benzene in the first extraction. The entire gram is therefore distributed between one volume of water and one-half volume of benzene in which only one gram of solute can dissolve, that is, the entire solubility in one-half volume benzene is the same as in one volume of water. The solute will then be equally distributed between water and benzene, or one-half gram will be extracted the first time. Similarly, one-half of what remains in the water will be extracted by the second half volume of benzene, and the total amount removed by the operation in two steps will be  $0.5 + 0.25$ , or  $0.75$  gram instead of  $0.67$  gram as before.

**Summary.**—The solubility of a substance in two immiscible solvents is not altered when the two solutions are brought together. The distribution of the amount dissolved can be shown by the distribution constant, or partition coefficient,  $K_{\text{dist. coef.}}$ .

This characteristic is made use of in extracting a substance by means of a more effective solvent. Extracting with portions of a solvent is more efficient than adding it in one single amount.

### EXERCISES

1. Two grams of a certain substance will dissolve in 100 cc. of solvent *A*, and 10 grams in the same volume of solvent *B*. *A* and *B* are not mutually soluble. Now suppose we start with 100 cc. of a saturated solution of *A* and

add 100 cc. of *B*, containing none of the solute. After the two solutions have been shaken together, how much of the substance will remain in *A*?

2. Suppose we now remove *B* in question 1, with its dissolved material, and again add another 100 cc. of *B* to *A* with its residual amount of solute. After shaking a second time, how much of the solute will still remain in *A*?

3. Repeat the extraction for a third time. After drawing a curve to show the amount extracted each time, what conclusion can you draw about the effectiveness of further extractions?

### COLLOIDAL SUSPENSIONS

Milk is impossible to filter with ordinary laboratory paper; and so you will find some of your precipitates, much to your disgust. The trouble is that your precipitate is so finely divided that the filter paper will not screen it out. If your solution contains bismuth trichloride and you dilute with water, a **colloidal suspension** of bismuth oxy-chloride results, and the particles are so small that they cannot be filtered out and neither will they settle. Colloidal suspensions are between larger suspensions, which will settle out within a reasonable time, and true solutions.

It often happens that the presence of a colloid can only be detected in a strong beam of light (the Tyndall effect), but in laboratory procedure if the colloidal suspension is not shown by a turbidity there is not much to worry about.

If a precipitate cannot be removed at its proper place in analysis the results may be disastrous in two ways: first, you are losing what you should remove and test; and second, the precipitate, going to a later place in the scheme of analysis, causes trouble by its presence where it is not provided for.

Colloids are really molecular aggregates and carry very weak electrical charges, either plus or minus. We might consider the units, from an electrical point of view, to be like ions with a one-thousandth valence or so. It is fortunate, however, that the particles are charged, because by adding ions or other colloids of opposite charge we can reduce the charges on the colloidal suspension, and, when the electrical charge has been reduced to a certain critical degree, the colloidal suspension will precipitate in the form of aggregates large enough to filter. Since most colloidal suspensions are negatively charged and readily take on  $H^+$ , a drop or two of the proper acid, with subsequent warming or boiling, will usually clear up the suspension. A few cubic centimeters of a solution of a neutral salt, as  $NH_4Cl$ , upon warming, will often very successfully

cause precipitation by neutralizing the charge on the suspension. Adding too much strong mineral acid will clear up the solution by putting the particles in true solution. You do not want the solution cleared up that way. Always try a double filter of two pieces of filter paper before resorting to the precipitation methods just described.

A colloidal suspension can often be prevented by using hot dilute solutions and adding the precipitating agent slowly and with constant stirring.

Do not infer that certain substances always appear as colloidal suspensions. This is a state or condition which many substances may assume under the proper conditions, and which is to be avoided in analytical procedure.

**Summary.**—Colloidal suspensions are finely divided aggregates of solid matter that are electrically charged and do not settle out.

The electrical charges may be  $+$  or  $-$  but are very small compared with ionic charges.

Colloids are precipitated by adding colloids or ions of the opposite sign.

The methods of preventing colloids in analytical work are better than those of removing them when once they have been formed.

A colloidal suspension is a state of suspension, not a specific property.

### EXERCISES

1. As you proceed with your laboratory work, make a list of precipitates that form colloidal suspensions, recording the best method that you find to precipitate each one.

2. If you will consult Holmes' "Laboratory Manual of Colloid Chemistry," 1928, you can determine in greater detail the conditions that will usually bring about a colloidal suspension.





A glimpse of early laboratory procedure; Liebig's laboratory, 1846.



## PART II

### THE METALLIC RADICALS OR CATIONS

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#### CHAPTER I

#### LABORATORY PROCEDURE IN GENERAL

**Desk Arrangement.**—Before starting the preliminary reactions it is necessary to become thoroughly familiar with every piece of apparatus and its use. Consult the list in Part V as you check over your supplies. Clean everything and keep it clean. If it is found that water will not remove the impurities from glassware and porcelain vessels, try a little dilute nitric or hydrochloric acid. Where there are organic chars, a **special cleaning solution** of solid sodium dichromate and sulfuric acid is very efficient. When acids are employed for cleaning purposes, use them sparingly. About 5 cc., carefully rinsed around the inside of a flask, can then be poured into another vessel, and so on until several have been cleaned. Finally dispose of the acid in a special acid crock so placed that the fumes will not contaminate the air in the laboratory. Sometimes a laboratory is provided with special fittings which will permit the acid to be poured directly into the sink while a good stream of water is flowing. Do not do this, however, unless your instructor specially permits it to be done. After being rinsed with water, the articles can be placed on a drying rack to drain or dry completely. At least drain everything before placing it in the desk.

In certain localities the tap water is badly contaminated with compounds of calcium or iron. Where this occurs a small amount of **distilled water** must be used for a final rinsing. The same caution must be applied in making up solutions and in the addition of water to a solution where a greater dilution is required.

The clean apparatus should be carefully arranged in the com-

partments of the desk, the glassware being placed in one compartment and the ironware and burner preferably in a lower section. A particle of iron rust getting into a flask will certainly give a test for iron later. If clean papers are placed in the glassware compartment, the danger of contamination from dried-up solutions in the wood will be avoided. It is a good plan, once in a while, even though the glassware looks clean, to give it an acid cleaning. Many times there will form a glaze, especially of the metallic sulfides, which cannot be removed with water. Later, when an acid is added in the course of experimentation, a test for the metal will result, although none has intentionally been put into the solution. Notice, from the photographs included in the text, how carefully and neatly everything is arranged in a commercial or research laboratory. Ionic inoculation is just as dangerous as pathogenic to the analyst.

You must keep some of your test tubes and certain pieces of apparatus **carefully marked**. You may remember to-day what is in the right-hand vessel, but to-morrow, if you have forgotten, aggravating results may follow. Very small labels are useful, but they become detached, so whenever possible obtain apparatus with a small frosted or roughened spot that can be easily marked with a pencil. The rims of porcelain crucibles and evaporating dishes are usually unglazed, and small pencil dashes can be made clearly visible on this roughened edge. Glassware should be, as far as possible, of the non-soluble variety. Ordinary glass is attacked by reagents, especially alkalies, and a contaminated solution is the result.

In removing solutions from reagent bottles, never lay the stopper down. Hold it between the fingers of one hand in the manner that you find most convenient by practice, and return it to the proper bottle. Never pour back into a reagent bottle any excess which you may have taken. It is a method of complimenting the cleanliness of your glassware in which your fellow-students, and especially your instructor, will not participate. In many laboratories you would be excluded for a period of time, if not altogether, if caught returning a solution to a reagent bottle.

Never remove stock bottles to your own desk. They are for the use of all. Your own individual reagent bottles are on the shelves on your desk, and since you are to use your set of reagents dozens of times in the course of a semester, it will save a lot of time

if you arrange them in a definite order, and keep them so arranged. It is a time-consuming and perfectly useless occupation to read back and forth along a line of reagent bottles, when a little system would make identification the matter of a moment.

**Precipitation.**—Precipitation is accomplished by adding the precipitating agent either in small portions or dropwise. A small Erlenmeyer flask makes an ideal vessel in which to precipitate, because there is no danger of loss by spattering. Also, between additions of the precipitating agent, the solution can be efficiently mixed by a rotary motion of the flask. Three or four rotations will do more than five minutes' stirring with a glass rod; and then there is no rod to clean later. An excess of reagent usually means a little more than is just sufficient to cause complete precipitation. If between additions of reagent the precipitate is allowed to settle a little, when the next addition is made it is very easy to see whether more precipitate forms or whether the reagent enters without producing any effect. Some prefer tilting the flask and adding the reagent by running it down the side. Where an acid or base is the precipitating agent and litmus paper is used to determine an excess, never throw a small piece into the solution. Litmus test strips consist of an uncoated paper which has been soaked in a solution of litmus and then dried. When the paper is left in the solution for several minutes, the dye will be washed out, with a consequent color reduction. This color change does not indicate a change of acidity or alkalinity. Preferably, wet a glass rod and place a moist piece of litmus paper on it so that about  $\frac{1}{8}$  inch extends below the lower end of the rod. Now lower the rod so that the paper tip touches the liquid, and withdraw it instantly. The result can be quickly seen and the tip of paper, when torn off, leaves another section of paper to be used for the next test. It is not necessary to use a whole strip of paper for one test, and the surface test should be the same as that at the bottom of the flask.

Do not judge alkalinity where ammonium hydroxide is concerned by the smelling method. After adding this reagent, even in small amounts, and stirring thoroughly, the air near the mouth of the flask will smell of the gas, while at the same time the litmus test of the solution may show acidity. Since many precipitates will not form in acid solutions, an error in this direction would be disastrous.

One common error made in early precipitation work is to add



the reagent and have a precipitate form in the upper part of the solution. The solution is not stirred at the time, and there is an excess of reagent at the top only. When the whole thing is properly mixed, however, the precipitate vanishes, simply because the solution as a whole did not contain excess of reagent. Remember to precipitate the entire solution, not a part of it.

**Types of Precipitates.**—The most common method of identifying a precipitate is by its color, although the type of precipitate may be at times of some assistance. A precipitate of silver chloride, for example, is **curdy**; of lead chloride, **crystalline**; of lead sulfate, **sandy** or **granular**; of aluminum hydroxide, **gelatinous**; of arsenious sulfide, **flocculent**. Microscopic examination of these masses has shown that they are all made up of crystals, some exceedingly small and others large enough to be distinguished by the naked eye. Crystal structure can often be made apparent by holding in the sunlight or other strong light. A characteristic sparkle will result.

**Change in Type and Color of Precipitate.**—The type of precipitate and sometimes the color depends upon the concentration of reagents used, the amount of stirring, the temperature, and the degree of insolubility of the precipitate formed. The more rapidly a precipitate is formed the smaller will be the crystals. Large crystals come from a dilute solution, but they are formed slowly and must, therefore, be given plenty of time to develop. A flocculent precipitate contains flocs of microscopic crystals, and in a curd or gel there is a regular mat or felt of the particles containing more or less of the liquid portion.

From this discussion it can be seen that the identification must not be based entirely upon the type of precipitate. While it is true that silver chloride usually forms curds, and arsenious sulfide flocs, with calcium oxalate and ammonium magnesium phosphate it is different. Although the usual characterization of the precipitate is crystalline, these two substances very frequently come down as flocculent masses, especially where the volume of solution has been concentrated by boiling. If you have been looking for crystalline precipitates, meaning, of course, the type that can be seen with the naked eye, you would be inclined to report negatively when a flocculent mass appeared. For this reason the solubility in some acid is determined, to assist in making a final decision.

It frequently happens that a precipitate, upon standing, will change in character due to the difference in solubility of large and small crystals. The smaller the crystal the more soluble it is, so that a flocculent precipitate is more unstable than a large crystalline one, and upon standing a few hours a radical change may take place. The slow formation of large crystals from dilute solutions is often started by rubbing the inside of a test tube a few times with the end of a broken glass rod. Where the large crystalline type of precipitate is likely to be formed, the solution under no circumstances should be discarded until it has stood for at least twenty-four hours.

In judging the amount of a radical present in a precipitate, our conclusions may be very erroneous unless we take into consideration the type of precipitate involved. For example, an amount of lead that would give a copious precipitate when in the form of flocculent lead chromate would, in white granular lead sulfate, give an amount so small as to be easily overlooked in the bottom of the vessel, and particularly if it were in a white crucible.

Since a precipitate, upon standing, can change in size of particle, it is not surprising to find that the character of the color may also be altered. For example, lead chromate, when precipitated rapidly from a cold solution, will frequently come down very finely divided and nearly white. Upon standing the color will deepen and finally assume its usual shade of yellow (see Plate I, *D* and *E*). In qualitative analysis, as elsewhere, "a little knowledge is a dangerous thing"; if you are expecting, in the course of analysis, a precipitate of a certain color and type, and something else appears, do not draw conclusions until you have made sure that it is not the thing you are looking for after all, but in an unusual condition. Make your work in analytical chemistry so exact that a precipitate at a particular point in analysis can have but one meaning.

**Washing Precipitates.**—Many precipitates, especially where voluminous, can best be washed in the flask before filtering. Water cannot easily penetrate a mass of precipitate after it has become consolidated on the filter paper during filtration. In **washing by decantation**, the solid matter is permitted to settle, and the liquid almost entirely poured off by carefully inclining the vessel. In this operation, a flask is usually more efficient than a beaker. More water is again added and, after settling, the liquid is poured off.

Finally the precipitate is transferred to the filter where it can be washed by a jet of water from a wash-bottle.

**Filtration.**—The simplest method of filtering employs a glass **filter funnel and filter paper**. The paper is folded twice, the seams well creased, and one of the quadrants opened out so that a cone results. The paper is now placed in the funnel, wet with water and firmly pressed down so that no air bubbles remain back of it. Be sure that the seam is pressed well against the glass, otherwise a column of air will be drawn down and the filtering process made very slow. The bottom of the funnel stem is cut at an angle so that the liquid can run off readily. The discharge will also be hastened by placing the end of the funnel stem against the side wall of the vessel into which the liquid is draining. Time will also be saved if most of the liquid is poured through first, and finally



FIG. 6.—Reinforcement of Base of Filter Paper with a Small Square of Cheesecloth to Prevent Breaking When Suction is Used.

the precipitate transferred. The last of the precipitate from the flask can be rinsed out. Where a flask is used there will be practically no spattering. In using a beaker, a glass rod held across the top and over the lip of the beaker will direct the course of the liquid. Never allow the filter paper to become covered with liquid as it may drain down the back of the paper. One-fourth inch is the least that should be allowed between the surface of the liquid and the top edge of the paper.

Where the precipitate is very compact, and gravity filtration would consume too much time, a **filter flask** with a suitable means of **suction** is used. The paper must now be reinforced with a perforated platinum cone or a small square of cheesecloth folded at the base of the filter paper (see Fig. 6). In using a wash bottle always direct the stream of water along the top of the precipitate in the paper so that it is washed down into the point. This will not only

wash all of the precipitate but will also make subsequent transfer easier to accomplish.

Much valuable time may be saved by using a filter paper of proper compactness or filtering power. In filtering a coarse precipitate, a very compact paper, which might be used to advantage with a precipitate of very finely divided barium sulfate, is not only unnecessary in filtering capacity but will filter with extreme slowness. Choose a paper that will not permit solid particles to go through but will be loose enough in texture to filter rapidly.

A precipitate should never be allowed to dry out. The solids may become very hard and subsequent solution will be slow and often incomplete. To keep moist, invert the funnel and paper in a beaker partly filled with water as shown in Fig. 7.

#### Transfer of Precipitate.—

Very frequently the precipitate, after washing, is dissolved on the filter paper by pouring the solvent through and catching the solution in a test tube. By pouring this same solution back on the filter paper one or more times, complete solution may finally result, and with the use of a minimum amount of solvent. This practice is followed only where the precipitate is quite soluble and there is not much of it.

Where there is much volume to the precipitate it would take too long for the solvent to work through the precipitate while on the paper, and for that reason it is transferred to an evaporating dish. To do this, open the filter paper and scrape the precipitate off by means of a porcelain spatula. Never use a knife just because it may be more convenient than the spatula. A jet of water from the wash-bottle will now wash the precipitate into the evaporating dish or casserole. Never soak a paper in a solvent, because a mass of paper pulp will usually result. If the precipitate is very small, the outer edges of the filter paper can be

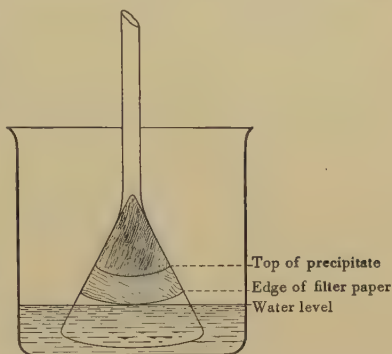


FIG. 7.—Method for Keeping a Precipitate Moist.

The filter funnel with paper and precipitate is inverted in a beaker partly filled with water. The water level must not reach the precipitate.



torn off and discarded and the paper containing the precipitate placed in an evaporating dish with a little water. By stirring with a glass rod, the precipitate can be washed out and the paper removed before any acid or base is added.

Sometimes it is more convenient to punch a hole in the bottom of the filter paper before it has been removed from the funnel, and to wash down the precipitate by a stream of water.

**Dissolving the Precipitate.**—Where there are special instructions given in the procedure for dissolving a precipitate, they must be closely followed. As a rule, breaking up the mass of precipitate with a glass rod is preferable to using solvents of a high concentration or unnecessary heating. The student who always brings about solution by using the strongest solvent and then boiling is not going to get anywhere in analytical chemistry. Very seldom does a certain solvent attack any one substance and not another. Solution is very largely a matter of degree, and conditions must be controlled if one substance is to be separated from another.

**The rate of solution** is another important factor that must be taken into account, especially in dissolving mixed precipitates. The solubilities in water in moles per liter of the sulfides of cobalt, nickel, manganese and zinc at  $18^{\circ}$  are as follows:  $\text{CoS}$ ,  $1.7 \times 10^{-13}$ ;  $\text{NiS}$ ,  $1.2 \times 10^{-12}$ ;  $\text{MnS}$ ,  $3.7 \times 10^{-8}$ ;  $\text{ZnS}$ ,  $3.5 \times 10^{-12}$ . The solubilities of all are increased as the solvent is made acid with hydrochloric acid, but the ratios are not changed by a large amount. However, when a 10 per cent solution of hydrochloric acid is added to the mixed sulfides, it will be found that at the end of ten minutes the manganese and zinc sulfides are completely dissolved while those of cobalt and nickel are scarcely attacked.

The rate of solubility, then, is just as important as the final solubility in separating substances. In this last example, if the solvent action of the acid had continued long enough, the entire mass would have been put into solution, and no separation thereby made. Solubility tables consist of maximum solubilities, and the element of time to reach that state of equilibrium is not considered, but it must be seriously reckoned with in analytical separations.

**Concentration of Filtrates.**—Filtrates are usually voluminous, because of the original volume of solution and the added washings which may contain valuable material. Or again, the filtrate may contain some volatile substance that may interfere with subse-



quent reactions. In either case, the solution can be boiled in a large-surfaced open container, such as a casserole or evaporating dish, until the steam coming off gives no further test of the volatile substance. Concentrating can be continued, when necessary, to about 10 cc. by boiling rapidly. When this volume is reached, it is preferable to reduce the flame and cover the evaporating dish with a watch glass. The steam can now escape by means of the lip.

In evaporating to a smaller volume, say 3 cc., the flame must be very low and luminous, otherwise spattering will result. Where dryness is required, the flame must be withdrawn before all of the liquid has disappeared. If this is not done, the solid may become overheated and decompose, with a possible loss of volatile matter.

**Ignition.**—Sometimes there are volatile compounds present in the solid residue that it is desirable to eliminate by heating to a high temperature. To ignite the residue means to heat the solid in a crucible or evaporating dish to a specified temperature. If the instructions state a dull red heat, use a flame that will heat the bottom of the crucible to a dull heat and no more. A higher temperature no doubt will drive off more than is desired. Above all things, do not introduce the flame into the crucible from above. This is not an efficient method of igniting as it usually drives the volatile compound back into the crucible, and it may also introduce harmful substances.

**Record of Experiments.**—There is much latitude in keeping experimental notes and in making reports. No one, however, will question the following basic principles: (a) Enter notes, briefly but clearly on a sheet of paper either in a bound book or a loose leaf. Have the sheet on your desk as you are experimenting, and enter the results at the time you obtain them. (b) Number the operations to correspond to those in the text so that they can be correlated at any future time. (c) Answer the questions proposed in a certain operation before going on to the next. They undoubtedly have an important bearing upon what follows. (d) Write the equations in ionic form as far as possible and use the conventional devices that were introduced in the theoretical section. (e) Make frequent reference to Part I. A happy balance between theory and practice will make for the highest efficiency.

## CHAPTER II

### THE SCOPE OF INTRODUCTORY QUALITATIVE ANALYSIS; SEPARATION OF RADICALS INTO GROUPS

Although it was stated in the introduction that qualitative analysis has for its purpose the determination of what, and not how much, is present in a substance under examination, certain limitations must now be proposed since this is an introductory course in the subject.

A total of ninety elements have been identified (see list of elements and their atomic weights, in Table XXV), but many of these are of very limited occurrence and would be found only as an occasional trace. Scandium, iridium and rhodium might be used as examples of this group of comparatively rare elements. There is also a second group which consists of elements that are found in larger amounts than traces, but their identification involves a special set of tests that would not regularly be included in a beginning course. Gold and platinum might be included in this list. After an introductory course has been completed, no special difficulty should be experienced, however, in making many of the more involved tests associated with these two classes of elements.

Outside of the radicals requiring special consideration, there are a number of elements of frequent occurrence in metallic and non-metallic radicals. These occur either alone or in combination, and are the ones included in this course. A complete list of the radicals includes the following:

**Metallic Radicals, or Cations.**— $\text{Pb}^{++}$ ,  $\text{Ag}^+$ ,  $\text{Hg}_2^{++1}$ ,  $\text{Hg}^{++}$ ,  $\text{Cu}^+$  and  $\text{Cu}^{++}$ ,  $\text{Bi}^{+3}$ ,  $\text{Cd}^{++}$ ,  $\text{As}^{+3}$  and  $\text{As}^{+5}$ ,  $\text{Sb}^{+3}$  and  $\text{Sb}^{+5}$ ,  $\text{Sn}^{++}$  and  $\text{Sn}^{+4}$ ,  $\text{Fe}^{++}$  and  $\text{Fe}^{+3}$ ,  $\text{Cr}^{++}$  and  $\text{Cr}^{+3}$ ,  $\text{Al}^{+3}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Mn}^{++}$  and  $\text{Mn}^{+3}$ ,  $\text{Zn}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ .

<sup>1</sup> Research involving potential measurements with the calomel cell indicates that the mercurous radical is  $\text{Hg}_2^{++}$  and not  $\text{Hg}^+$ .

**Non-Metallic Radicals, or Anions.**— $\text{NO}_2^-$ ,  $\text{S}^-$ ,  $\text{SO}_3^-$ ,  $\text{S}_2\text{O}_3^-$ ,  $\text{CO}_3^-$ ,  $\text{SO}_4^-$ ,  $\text{PO}_4^{-3}$ ,  $\text{BO}_3^{-3}$ ,  $\text{BO}_2^-$ ,  $\text{B}_4\text{O}_7^-$ ,  $\text{SiO}_3^-$ ,  $\text{F}^-$ ,  $\text{C}_2\text{O}_4^-$ ,  $\text{C}_4\text{H}_4\text{O}_6^-$ ,  $\text{CrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^-$ ,  $\text{AsO}_3^{-3}$ ,  $\text{AsO}_4^{-3}$ ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $[\text{Fe}(\text{CN})_6]^{-3}$ ,  $[\text{Fe}(\text{CN})_6]^{-4}$ ,  $\text{SCN}^-$ ,  $\text{NO}_3^-$ ,  $\text{C}_2\text{H}_3\text{O}_2^-$ .

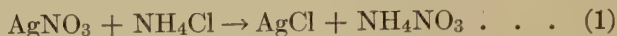
Sometimes a distinction is made between **proximate analysis**, in which the composition by groups is determined, and **ultimate analysis**, in which the composition by individual elements is the main purpose. In this procedure we shall combine the two methods as far as possible. For example, if chromium is present, we shall endeavor to determine whether it was originally in the substance as the metal  $\text{Cr}^0$ , a salt containing  $\text{Cr}^{+3}$ , a chromate containing  $\text{CrO}_4^-$  or a dichromate containing  $\text{Cr}_2\text{O}_7^-$ .

An approximation of the amount of radical present in an unknown can be made, if in the preliminary tests solutions are used in which a known concentration of radical and reagent is present. A comparison can then be made later of the amount of precipitate obtained in the analysis of a sample, with that obtained in the preliminary work. Our test solutions, unless otherwise stated, will always contain 10 milligrams (mg.) of radical per cubic centimeter of solution. The concentration of reagents will be given in terms of **n** or **m**, which were reviewed in the introduction.

It cannot be over-emphasized that the interpretation of results must be based upon concentrations of test solutions and reagents used. One of the greatest mistakes of the beginner in analytical procedure is to assume that the presence of radical "A" can be determined by adding "some" of a particular reagent, and that radical "B" can correspondingly be determined by the addition of another reagent. By considering the solubility-product principle it is evident that it is primarily a question of the product of ion concentrations exceeding  $K_{\text{SP}}$  and not of two substances getting together. When a specific reagent is added to a solution and no characteristic test results it does not necessarily follow that the radical is not present at all, but it does show that it is not present in sufficient concentration to give a test with the strength of the reagent used. Only where the preliminary work has been correctly done can analytical tests be correctly interpreted.

## THE SELECTION OF EQUATIONS TO REPRESENT REACTIONS

Four types of equations are in use to represent in part a chemical reaction. They are:



Each type has its advantages and disadvantages. (1) gives the reacting molecules only and involves no facts of ions or ionization. (2) is a pseudo-ionic equation, that is, it represents the manner in which the molecules ionize but does not express the ions themselves. One objection to this method is made on the ground that in  $\text{NH}_4^+\text{Cl}^-$ , for example, which basically represents a molecule of ammonium chloride, the valence relationships in molecular  $\text{NH}_4\text{Cl}$  are not as shown. (3) represents the ions that take part in the reaction, but this method becomes too involved when the molecules in an equation become numerous. (4) involves the principal ions in a reaction if we are justified in concluding that the ions forming a final precipitate are the most important ones.

It is not desirable or practicable to use a particular type of equation throughout a text and we shall therefore select the one that seems to emphasize best the main purpose of the reaction. The single arrow ( $\rightarrow$ ) and the double arrows ( $\rightleftharpoons$ ) will also be used with the same point in view. While it is true that practically all reactions are reversible, the double arrow will only be used when it is desirable to show that the products set up a reverse action to an extent that should be considered when we are dealing with the entire reaction.

## QUESTIONS THAT ARE INCORPORATED WITH THE PRELIMINARY TESTS

Two types of questions are included in each section of preliminary tests. The first are used to emphasize certain phases of the test that is being made, or to suggest a question that will be devel-



oped in the next reaction. These questions should be answered as the laboratory work is being done because their main purpose is to emphasize and prepare the way.

A second group of questions is placed at the end of each section under the title "Exercises," and will usually require more time for a careful consideration than can be permitted to interrupt the laboratory work. These questions aim to apply the theoretical principles of analytical chemistry to the specific reactions that are under consideration.

### SEPARATION OF THE CATIONS INTO GROUPS

To the uninitiated in analytical procedure, the ideal analysis would consist of taking 1 cc. of the sample and, by adding a few drops of a special reagent, obtaining a characteristic precipitate or colored solution that would always indicate the presence of a certain radical. While it is true that several special compounds, usually of a complex organic nature, have been made available for testing purposes, their general use by beginners is not desirable.

The use of special reagents in analysis usually requires a very exacting set of conditions, as concentration and temperature, and the beginner, of course, is usually lacking in the required skill to meet this situation. Many of the special reagents are, moreover, very unstable and must be made up frequently and tested daily.

The general procedure, then, in the absence of unit testing, is first to divide the metallic or non-metallic radicals into groups, and later to take each group and further subdivide it until finally end tests are obtained for each radical. The end test is frequently followed by a confirmatory test where it is considered that the end test is not sufficiently conclusive. With the cations, the division into groups can be made with a large degree of success, but we shall find later that the anions do not lend themselves as rigidly to group classification, and the unit testing in the original solution is resorted to more frequently.

In the grouping of metals for analysis, the arrangement followed by the periodic classification suggests itself because it has so often been emphasized in the study of the elements. In qualitative grouping, however, it will be found to be of very little assistance.

Groups are separated from the main solution by precipitation, and this means that the solubility characteristics of the members



are quite similar, at least in so far as they pertain to a particular precipitating radical. Likewise, in subdividing the group, as the analysis proceeds, use is made of similarities or dissimilarities of solubilities in given reagents. We have found that the periodic classification is not based upon solubility relationships, but involves atomic weights and certain chemical characteristics, for example, the acid-forming and base-forming properties. Furthermore, one particular valence with several of the radicals is unduly emphasized. Undoubtedly the relationships shown in the periodic classification have some bearing upon solubility, but there are so many other factors that the table is of little value in qualitative solubility separations. Solubilities are determined experimentally, and solubility tables are the best source of information in deciding why certain groups are constituted as they are, or in formulating other classifications or groupings.

The cation grouping will be considered as follows:

**Group 1. The Hydrochloric Acid, or Insoluble Chloride Group.**<sup>2</sup>— $\text{Pb}^{++}$  (in part only),  $\text{Ag}^+$ ,  $\text{Hg}_2^{++}$ .

**Group 2. The Hydrogen Sulfide, or Acid Sulfide Group.**—Subdivision A.— $\text{Hg}^{++}$ ,  $\text{Pb}^{++}$ , (the remainder from Group I),  $\text{Cu}^{++}$ ,  $\text{Bi}^{+3}$ ,  $\text{Cd}^{++}$ . Subdivision B.— $\text{As}^{+3}$ ,  $\text{As}^{+5}$ ,  $\text{Sb}^{+3}$ ,  $\text{Sb}^{+5}$ ,  $\text{Sn}^{++}$ ,  $\text{Sn}^{+4}$ .

**Group 3. The Ammonium Sulfide, or Alkaline Sulfide Group.**—Subdivision A.— $\text{Fe}^{+3}$ ,  $\text{Mn}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ . Subdivision B.— $\text{Al}^{+3}$ ,  $\text{Cr}^{+3}$ ,  $\text{Zn}^{++}$ .

**Group 4. The Ammonium Carbonate, or Alkaline Earth Group.**— $\text{Ba}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ca}^{++}$ .

**Group 5. Magnesium, and the Alkali or Soluble Group.**— $\text{Mg}^{++}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ .

There are other methods of grouping the cations, and in the sections covering the individual groups there will be found some of the more important variations. The grouping given above is the one most commonly employed, however.

It is also essential to note that the grouping just given will result only if the group reagents are added in the order given. A group must, therefore, be separated in its turn or a grand mix-up

<sup>2</sup> Since all precipitates have a certain small solubility, the term insoluble will be used in our experimental work to denote a specific limited solubility, the extent of which must be determined from preliminary tests or by reference to solubility tables.

will result. A certain group will precipitate only on the assumption that there are present in solution, at the time, a limited number of radicals. Do not attempt to take the carbonate group out first; it will have many companions.

#### PRELIMINARY EXPERIMENT SHOWING METHOD OF SEPARATING GROUPS

Usually there is not sufficient time to permit the testing of solutions of all of the metallic radicals to determine which ones have insoluble chlorides, which have sulfides insoluble in a solution of a given acidity, etc. The principle involved in group separations can, however, be shown by taking a solution containing one member from each group.

We shall, then, make up a solution containing 5 cc. each of test solutions (10 mg. per cc.) of  $\text{AgNO}_3$ ,  $\text{HgCl}_2$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{BaCl}_2$  and  $\text{KNO}_3$ .

Place the solution in a precipitating flask,<sup>3</sup> precipitate with 3*n*  $\text{HCl}$  added dropwise and in excess, and filter by gravity through filter paper.<sup>4</sup> Wash once with a small amount, about 3 cc. of cold water, and add washings to the filtrate. The precipitate on the filter paper represents Group I. Pour the filtrate and washings which contain the succeeding groups into a 300-cc. flask,<sup>5</sup> dilute with 150 cc. of water, and slowly bubble  $\text{H}_2\text{S}$  through the solution for about five minutes. Do not insert the rubber tubing connected with the gas supply directly into the solution, but connect it to a piece of glass tubing and place this in the solution. Be sure to wash the glass tube before it is used again, employing acid if necessary to clean it thoroughly. Contamination of your next solution may otherwise result. A more detailed and better method for precipitating with  $\text{H}_2\text{S}$  will be given in connection with Group II, but this will accomplish all that is desired at this

<sup>3</sup> The proper methods of precipitating, filtering, etc., were described in detail at the beginning of Part II. They will not be described again unless a special modification of the general procedure is to be made. You must therefore turn back, whenever it is necessary, to refresh your mind on any detail.

<sup>4</sup> It is to be understood that this is the method of filtering unless otherwise stated.

<sup>5</sup> Unless otherwise stated, the conical or Erlenmeyer type of flask is to be used.

point. Now filter and wash once with warm water. The precipitate represents Group II. The filtrate and washings are placed in a casserole or evaporating dish and boiled down to about 50 cc., cooled and poured into a 200-cc. flask. Any turbidity caused by free sulfur can be filtered off by using two thicknesses of paper. The sulfur is discarded. After 2 cc. of  $3n$   $\text{NH}_4\text{Cl}$  have been added the solution is made alkaline with  $\text{NH}_4\text{OH}$  (use litmus), and 4 cc. of  $6n$   $(\text{NH}_4)_2\text{S}$  added. Wash precipitate twice by decantation and filter. The precipitate represents Group III. The filtrate and washings are now concentrated to about 10 cc. and cooled, and any further precipitate discarded. Make the clear filtrate alkaline with  $\text{NH}_4\text{OH}$ , and add 5 cc. of the next group reagent,  $6n$   $(\text{NH}_4)_2\text{CO}_3$ . This precipitate is sometimes slow in forming, so if a turbidity alone appears, the solution should be set aside for an hour. Filter and wash once with cold water. The precipitate represents Group IV, and the last group is contained in the filtrate.

### EXERCISES

1. How could you test in a filtrate to determine if the group precipitating reagent had been added in excess?
2. Show by the common-ion effect the value of adding the group reagent in reasonable excess.
3. Sometimes, where the reagent is added in large excess, the precipitate has a tendency to redissolve. What must have been formed?
4. What is the harm in not adding the group reagent in excess?
5. Give two reasons for washing the precipitate.
6. Is it always necessary to add washings to the filtrate? (You might check up your answer a little later in the course.)
7. Why should any turbidity be removed before making a precipitation?
8. The  $\text{NH}_4\text{Cl}$  is added before precipitating Group III to prevent the premature precipitation of magnesium. What principle is involved?
9. Why is there not the danger of precipitating the barium, representing Group IV, as hydroxide in this practice solution that there was with the magnesium? (See solubility table.)
10. Why did the precipitate of aluminum hydroxide appear instantly while that of barium carbonate might have taken a greater period of time?
11. Can  $\text{NH}_4\text{Cl}$  be used to precipitate Group I? (Consider it both from the point of view of obtaining Group I precipitate, and also the introduction of radicals in the filtrate.)
12. What will be the effect of adding  $\text{H}_2\text{S}$  to our practice solution first? Suppose  $\text{NH}_4\text{OH}$  is the first added? (Consult solubility tables.)
13. The  $\text{H}_2\text{S}$  in the excess of reagent from Group III is boiled off before the next group reagent is added. Can you suggest the reason?

14. Is it always necessary to remove the previous group reagent? (Consider the HCl of Group I being present when the  $\text{H}_2\text{S}$  precipitation in Group II is made.)

15. If the barium were not precipitated until the fourth group reagent had been added, would this signify that it had not reacted before? (Starting with  $\text{BaCl}_2$ , show what reactions have taken place until the final precipitation occurred.)

### CHAPTER III

#### GROUP I.—THE HYDROCHLORIC ACID OR INSOLUBLE CHLORIDE GROUP

SILVER,	Ag; at. wt. 107.88; $\text{Ag}^+$
MERCURY(OUS),	Hg; at. wt. 200.6; $\text{Hg}_2^{++}$
LEAD,	Pb; at. wt. 207.2; $\text{Pb}^{++}$

This group consists of cations whose chlorides are insoluble in a neutral solution or with a slight excess of HCl.

#### PRELIMINARY TESTS

The reactions are arranged so that they naturally group themselves about the more important compounds that involve the radical under consideration. The precipitate that is formed with the group reagent is usually considered first. By this procedure the paragraph headings are the precipitates or other important compounds which will form later the basis of our analytical separations.

Where the reagents are used for the paragraph headings there results a practical duplication for all of the radicals studied. Emphasis should be placed upon the most characteristic compounds containing the radical under consideration and not upon a list of reagents. Suppose, for example, we are considering AgCl. In one paragraph, by our method, we shall consider how it is formed, its general characteristics and most important solubilities. This arrangement will surely accomplish more than that in which the precipitation of AgCl is considered under the heading "Hydrochloric acid" and one later finds that this substance is soluble in KCN in a paragraph with the reagent heading "Potassium cyanide."



SILVER-ION,<sup>1</sup>  $\text{Ag}^+$  (COLORLESS)

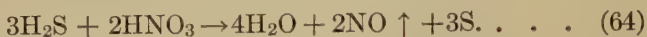
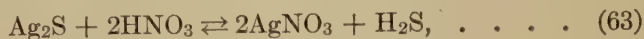
**1. Silver Chloride,  $\text{AgCl}$ .**—Take 5 cc. of a test solution of  $\text{AgNO}_3$  and precipitate with dilute  $\text{HCl}$ . Write the equation for the reaction. What is the color and type of precipitate? Decant off most of the liquid. Allow a small amount of the precipitate to stand in the sunlight or other strong light for a few minutes. A discoloration is the result of the  $\text{AgCl}$  being partially reduced by the light. The action is increased where organic matter is present. What is the source of the organic matter in your test solution? Heat another portion of the precipitate with the liquid and notice whether it dissolves appreciably. Look up its solubility. Did heating change the physical appearance of the precipitate? (A careful consideration of the points brought out now will be of great assistance in later identification.) Take another portion of  $\text{AgCl}$  and carefully add  $6n$   $\text{NH}_4\text{OH}$  until it dissolves. Soluble silver-ammonia chloride is formed. This contains the complex ion,  $[\text{Ag}(\text{NH}_3)_2]^+$ . Write the complete equation. Carefully add dilute  $\text{HNO}_3$  to the clear solution until it is just acid. The  $\text{AgCl}$  is reprecipitated. Solutions of  $\text{KCN}$  and  $\text{Na}_2\text{S}_2\text{O}_3$  (the "hypo" used in photography), are also solvents for  $\text{AgCl}$ . Add  $6n$   $\text{NaOH}$  to another portion of the  $\text{AgCl}$ . Does it dissolve? What does this show? Try the formation of  $\text{AgCl}$  by adding  $\text{NaCl}$  and  $\text{NH}_4\text{Cl}$  as precipitating agents to test solutions of  $\text{AgNO}_3$ . Can you suggest any special advantage that either of the three chlorides possesses in the precipitation of  $\text{AgCl}$ ?

**2. Silver Sulfide,  $\text{Ag}_2\text{S}$ .**—Take four test tubes and put in each 3 cc. of the test solution of  $\text{AgNO}_3$ . Make the first acid with a few drops of dilute  $\text{HNO}_3$ , make the second approximately neutral,<sup>2</sup> make the third alkaline with  $\text{NaOH}$ , and the fourth alkaline with  $\text{NH}_4\text{OH}$ . Slowly bubble  $\text{H}_2\text{S}$  through each solution until precipitation is complete. Interpret the results. If  $\text{Ag}_2\text{S}$  can be precipitated from an ammoniacal solution what does it show about the relative ionization of  $\text{Ag}_2\text{S}$  and  $[\text{Ag}(\text{NH}_3)_2]^+$ ? Try the solubility of the sulfide in cold dilute  $\text{HCl}$ . Carefully heat some of the pre-

<sup>1</sup> Silver-ion signifies the substance ionic silver and is now a commonly used word.

<sup>2</sup> A silver nitrate solution should be neutral, although from the radicals present you might suppose it would give an acid solution by hydrolysis. Solutions of commercial  $\text{AgNO}_3$  frequently do give acid solutions, not due to hydrolysis, but to traces of acid impurities.

precipitate with  $12n$   $\text{HNO}_3$ , adding more acid from time to time, if necessary to complete the solution. A white or yellow turbidity appearing is free sulfur resulting from the reactions which are shown by the following:



Remember that  $\text{H}_2\text{S}$  is decomposed by  $\text{HNO}_3$ , so that later you will not suggest this acid as one to be used in acidifying Group II before the  $\text{H}_2\text{S}$  precipitation. Would  $\text{Na}_2\text{S}$ , which is very soluble in water, precipitate  $\text{Ag}_2\text{S}$ ? How about  $(\text{NH}_4)_2\text{S}$ ?

**3. Silver Hydroxide,  $\text{AgOH}$ , and Silver Oxide,  $\text{Ag}_2\text{O}$ .**—Add dilute  $\text{NH}_4\text{OH}$  dropwise to a test solution of  $\text{AgNO}_3$ . The gray precipitate which forms and gradually darkens is a mixture of  $\text{AgOH}$  and  $\text{Ag}_2\text{O}$ . The very unstable  $\text{AgOH}$  quickly changes to brown  $\text{Ag}_2\text{O}$  as shown by:



By adding an excess of  $\text{NH}_4\text{OH}$  the precipitate will dissolve according to the following equation:



Repeat the experiment, using  $\text{NaOH}$  instead of the  $\text{NH}_4\text{OH}$ . Is there any difference in the rate of forming the  $\text{Ag}_2\text{O}$ ? Does it redissolve in excess?

**4. Additional Precipitates of Silver-ion.**—Silver chromate,  $\text{Ag}_2\text{CrO}_4$ , red; silver iodide,  $\text{AgI}$ , a light yellow; silver bromide,  $\text{AgBr}$ , a still lighter yellow, or almost white; silver cyanide,  $\text{AgCN}$ , white; silver phosphate,  $\text{Ag}_3\text{PO}_4$ , yellow. These are precipitates which will later find an important use in non-metallic analysis.

**5. Metallic Silver,  $\text{Ag}^\circ$ ,** is readily displaced (precipitated) from its solutions by many metals, as tin and lead. See electromotive series and note the position of silver.

## EXERCISES

1. Show how the extent to which  $\text{AgOH}$  has acid properties was illustrated in one of your experiments.

2. Will  $\text{AgCl}$  precipitate merely because you added a solution of a soluble chloride to one of silver nitrate, or is there more involved?

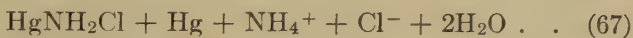
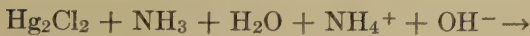
3. Write the instability-constant ratio for  $[\text{Ag}(\text{NH}_3)_2]^+$ , and show how the addition of nitric acid will precipitate  $\text{AgCl}$ . Where did the  $\text{Cl}^-$  come from? Why not add hydrochloric acid to furnish the acidity, instead of nitric acid?

4. A certain ammoniacal silver solution has a large excess of  $\text{NH}_4\text{OH}$ . When a few drops of  $\text{NaCl}$  are added there is but a faint turbidity of  $\text{AgCl}$ . If a few drops of  $(\text{NH}_4)_2\text{S}$  are now added there is a decided black precipitate of  $\text{Ag}_2\text{S}$ . Explain all of the theoretical principles involved and show also the practical bearing of the experiment on analytical procedure.

5. A precipitate of  $\text{AgCN}$  dissolves when an excess of  $\text{KCN}$  solution is added, giving the complex  $[\text{Ag}(\text{CN})_2]^-$ . What is the formula of the entire molecule? How would you determine experimentally whether this complex ion is more or less soluble than  $\text{Ag}(\text{NH}_3)_2^+$ ?

MERCUROUS-ION,  $\text{Hg}_2^{++}$  (COLORLESS)

**1. Mercurous Chloride,  $\text{Hg}_2\text{Cl}_2$  (Calomel).**—Take 3 cc. test solution of  $\text{Hg}_2(\text{NO}_3)_2$  and add dilute  $\text{HCl}$  dropwise. How does the precipitate of  $\text{Hg}_2\text{Cl}_2$  differ in appearance from that of  $\text{AgCl}$ ? Write the equation for the reaction. Test the solubility of a portion of  $\text{Hg}_2\text{Cl}_2$  in hot water and see also if there is any change in the precipitate on exposure to the sunlight. Try the solubility of another portion in dilute  $\text{HNO}_3$ .  $\text{Hg}_2\text{Cl}_2$  is slowly soluble in hot concentrated  $\text{HNO}_3$ ,<sup>3</sup> giving the nitrate. With hot aqua regia a solution of  $\text{HgCl}_2$  results. Refer to oxidation and reduction in Part I, and then write the equation for the reaction. Add  $\text{NH}_4\text{OH}$  to the remainder of the precipitate of  $\text{Hg}_2\text{Cl}_2$ . Describe the changes which take place. The reaction is as follows:



<sup>3</sup> Great care must be exercised in heating concentrated acids, especially in test tubes. They are likely to spatter or blow out explosively, because of gas formation. The experiment is not suggested here, so the facts are given instead. If you ever perform this or a similar experiment, heat very slowly and always hold the mouth of the test tube away from you. A better method is to place a little of the solid in an evaporating dish, cover with acid and then heat.

## PLATE II

### THE MORE IMPORTANT PRECIPITATES IN QUALITATIVE ANALYSIS

**A. White.** The term "white" applied to precipitates may be misleading. There is a difference between the opaque white of a precipitate of  $\text{AgCl}$  and the translucent gelatinous precipitate of  $\text{Al}(\text{OH})_3$ . The latter is sometimes referred to as a "dull white." Crystals of  $\text{MgNH}_4\text{PO}_4$  in some texts constitute "a crystalline precipitate"; while in others they are specifically characterized as white. Both may be correct because under certain conditions they will be perfectly clear and in others the structure will be such that the light is diffused and "white" is the result. White precipitates include:  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{HgNH}_2\text{Cl}$ ,  $\text{PbCl}_2$ ,  $\text{Pb}(\text{OH})\text{Cl}$ ,  $\text{PbSO}_4$ ,  $\text{Pb}(\text{OH})_2$ ,  $\text{Pb}(\text{CN})_2$ ,  $\text{Pb}_3(\text{PO}_4)_2$ ,  $\text{Hg}(\text{CN})$ ,  $\text{Bi}(\text{OH})_3$ ,  $\text{BiOCl}$ ,  $(\text{BiO})_2\text{SO}_4$ ,  $\text{BiPO}_4$ ,  $\text{Cu}_2\text{Cl}_2$ ,  $\text{Cu}_2(\text{CN})_2$ ,  $\text{Cd}(\text{OH})_2$ ,  $\text{Cd}_2[\text{Fe}(\text{CN})_6]$ ,  $\text{Cd}(\text{CN})_2$ ,  $\text{Sn}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{AlPO}_4$ ,  $\text{ZnS}$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{MgNH}_4\text{PO}_4$ , the hydroxides, carbonates, oxalates, fluorides, sulfates and sulfites of Ba, Sr and Ca,  $\text{AgCO}_3$ ,  $\text{AgSO}_3$ ,  $\text{Ag}_2\text{S}_2\text{O}_3$ ,  $\text{Ag}_2\text{C}_2\text{O}_4$ ,  $\text{Ag}_3\text{BO}_3$ ,  $\text{Ag}_3\text{SO}_4$ ,  $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$ ,  $\text{Ag}_2\text{CO}_3$ ,  $\text{AgSCN}$ ,  $\text{Ag}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{SiO}_2$ ,  $\text{BiONO}_3$ ,  $\text{Mn}(\text{OH})_2$ ,  $\text{Ba}_3(\text{PO}_4)_2$ .

**B. Cream.** This color is used in describing precipitates more or less interchangeably with "ivory," "light yellow," "flesh color," etc. It is not the intense light yellow of  $\text{As}_2\text{S}_3$  but contains a trace of red or reddish-brown. It is the characteristic color of  $\text{AgBr}$ ,  $\text{AgI}$ , and of several precipitates when first formed and which later darken into flesh color or reddish-brown.  $\text{MnS}$  and  $\text{HgCl}_2 \cdot \text{HgS}$  are examples.

**C. Seal Brown.** This is a dark reddish-brown and is the characteristic color of the precipitate of  $\text{Bi}_2\text{S}_3$ . Certain black precipitates when finely divided or when first formed are this color, as  $\text{CoS}$  and  $\text{CuS}$ .

**D. Black.** Black precipitates are:  $\text{Ag}_2\text{S}$ ;  $\text{Ag}_2\text{O}$ , black or grayish-black;  $\text{Hg}_2\text{S}$ ;  $\text{Hg}_2\text{O}$ ;  $\text{PbS}$ ;  $\text{HgS}$ ;  $\text{BiI}_3$ ;  $\text{Cu}_2\text{S}$ ;  $\text{CuS}$ ;  $\text{CuO}$ ;  $\text{NiS}$ ;  $\text{Ni}(\text{OH})_3$ ;  $\text{FeS}$ . Recall that certain black precipitates when first formed or finely divided may be brown.

**E. Light Yellow.** Many light yellow precipitates darken upon standing. The light yellow precipitates are:  $\text{PbI}_2$ ;  $\text{HgO}$ , also is red;  $\text{HgI}_2$ , changes to orange-red like  $\text{Sb}_2\text{S}_3$ ;  $(\text{BiO})_2\text{Cr}_2\text{O}_7$ ;  $\text{Cu}_2(\text{OH})_2$ , changes to red on boiling;  $\text{Cu}(\text{CN})_2$ , changes to an intense light green;  $\text{As}_2\text{S}_3$ ;  $\text{As}_2\text{S}_5$ ;  $(\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3$ ;  $\text{FePO}_4$ , nearly white when first formed;  $\text{BaCrO}_4$ ;  $\text{K}_2\text{PtCl}_6$ ;  $(\text{NH}_4)_2\text{PtCl}_6$ ;  $\text{Ag}_3\text{AsO}_3$ ;  $\text{Ag}_3\text{PO}_4$ .

**F. Orange-yellow.** Certain light yellow precipitates may darken to orange-yellow upon standing. Orange-yellow precipitates are:  $\text{PbCrO}_4$ ,  $\text{CdS}$ ,  $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$ .  $\text{Ag}_4[\text{Fe}(\text{CN})_6]$  is erroneously given as flesh color or orange-yellow. The precipitate is white but may be colored due to ferrieyanide contamination.

**G. Yellowish-brown.** This is the characteristic color of a precipitate of  $\text{SnS}$ .

**H. Light Yellowish-brown.** This is the characteristic color of a precipitate of  $\text{SnS}_2$ .



# PLATE II







**I. Pink.** This is the characteristic precipitate of nickel dimethyl glyoxime,  $\text{Ni}[(\text{CH}_3)_2\text{C}_2\text{NOHNO}]_2$ . In making the test for  $\text{Ni}^{++}$  the concentration is usually so small that a solution of the dissolved molecules results (see Plate V, A). The precipitate of  $\text{Co}(\text{OH})_2$  may be pink at first but quickly darkens to dark red or reddish-brown.

**J. Orange-red.** This is the characteristic color of precipitates of  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_5$ . Other precipitates are:  $\text{Cu}_2\text{O}$ , may have color changes from green, light yellow, orange to red;  $\text{Hg}_2\text{CrO}_4$ ,  $\text{Ag}_3[\text{Fe}(\text{CN})_6]$ .

**K. Reddish-brown.** This is the characteristic color of a precipitate of  $\text{Fe}(\text{OH})_3$ . Other precipitates are:  $\text{Ag}_2\text{CrO}_4$ , the color may be a more intense red like that of  $\text{Fe}(\text{SCN})_3$  in the concentration shown in Plate I, B;  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ , is darker than  $\text{Fe}(\text{OH})_3$ ;  $\text{Ag}_3\text{AsO}_4$ .

**L. Green Precipitates.** The precipitate photographed is  $\text{Cr}(\text{OH})_3$  which is a dark grayish-green or commonly referred to as "dirty green." It frequently is a dark bluish-gray with no suggestion of green. The precipitates of  $\text{Fe}(\text{OH})_2$  and  $\text{CrPO}_4$  are very similar to that of  $\text{Cr}(\text{OH})_3$ ; the latter may be a little lighter. The precipitates of  $\text{Ni}(\text{OH})_2$  and  $\text{Ni}(\text{CN})_2$  are a very light green, and that of  $\text{Cu}(\text{OH})_2$  is a light bluish-green. The precipitate of  $\text{HgI}$  is yellow at first but may change to green. Rinmann's green,  $\text{CoO} \cdot \text{ZnO}$ , is shown in Plate III, F.

**M. Flesh Color.** The precipitate photographed is  $\text{MnS}$ . Several light yellow or cream-colored precipitates may change to this color upon standing.

**N. Russet-brown.** This color is referred to as dark brown, chocolate, etc. It has no suggestion of red, as with  $\text{Fe}(\text{OH})_3$ . The precipitate photographed is  $\text{Mn}(\text{OH})_3$ . The precipitate of  $\text{Co}(\text{CN})_2$  is similar but quickly changes to the grayish-green of  $\text{Cr}(\text{OH})_3$  by hydrolysis if the solution is not sufficiently acid.

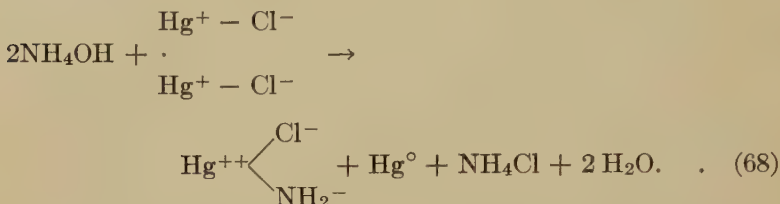
**O. Blue.** The precipitate photographed is ferrous ferricyanide,  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ , Turnbull's blue. The precipitate is a dark blue in contrast with Prussian blue which has a greenish shade. The precipitate of  $\text{CoAl}_2\text{O}_4$ , Thénard's blue, is shown in Plate III, E.

**P. Dark Greenish-blue.** Ferric ferrocyanide,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , Prussian blue. The difference between O and P is readily seen by diluting so that the suspensions are transparent.

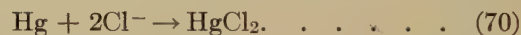
**Q.** The gradual change of color or "virage" of acid cresol red is shown from the deep red with  $p\text{H} = 0.2$  to the light-reddish yellow where  $p\text{H} = 1.8$ . The exact  $p\text{H}$  values are:  $a = 0.2$ ,  $b = 0.4$ ,  $c = 0.6$ ,  $d = 0.8$ ,  $e = 1.0$ ,  $f = 1.2$ ,  $g = 1.4$ ,  $h = 1.6$ ,  $i = 1.8$ .

The correct acidity for the precipitation of the  $\text{H}_2\text{S}$  group is  $0.3n$  which corresponds to  $p\text{H} = 0.8546$ . The color, therefore, with acid cresol red is between  $d$  and  $e$ . In order to adjust the solution to this acidity take a dropping bottle containing the indicator and place a few drops on a white porcelain surface. The solution for the  $\text{H}_2\text{S}$  precipitation is now diluted with 100 cc. of water and 1 drop is removed by means of a glass rod and mixed with 1 drop of the indicator. If the color is too yellow, more  $\text{HCl}$  is added; if too red, the solution is diluted with water and the solution again tested with the indicator.

The  $\text{Hg}^\circ$  is bluish-black. The mercuric-amino-chloride,  $\text{HgNH}_2\text{Cl}$ , is white and very infusible. The entire mass will vary from a gray to a black depending upon the amount of metallic mercury that has been formed. The structural formula of the white compound shows that part of the mercury in  $\text{Hg}_2\text{Cl}_2$  was oxidized:



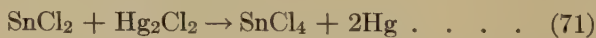
Transfer the black mixed precipitate to an evaporating dish, cover with aqua regia and warm until the precipitate has completely dissolved. The reactions are:



Write the equation to show how free chlorine comes from the interaction of  $\text{HNO}_3$  and  $\text{HCl}$  in aqua regia.  $\text{AgCl}$  and  $\text{Ag}$  are not soluble in aqua regia. If we have  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$  together and the  $\text{NH}_4\text{OH}$  treatment does not completely dissolve the  $\text{AgCl}$  on account of the large excess of mercury and mercury salts, do the last reactions suggest a method for freeing the  $\text{AgCl}$  so that it can be put into solution with  $\text{NH}_4\text{OH}$ ?

Add a few drops of a solution of stannous chloride,  $\text{SnCl}_2$ , to one of  $\text{Hg}_2\text{Cl}_2$ . Describe the change that occurs.<sup>4</sup>

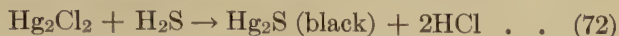
The reaction is:



What type of reagent is  $\text{SnCl}_2$ ? Can this reaction be carried out in the presence of free chlorine? For what radicals can this reaction be used as a test?

<sup>4</sup> Where no change takes place it is probably due to the stannous chloride solution having been oxidized to stannic chloride. See that the reagent bottle contains metallic tin.

**2. Mercurous Sulfide,  $\text{Hg}_2\text{S}$ .**—Pass  $\text{H}_2\text{S}$  into a solution of a mercurous salt. The final black precipitate is mercuric sulfide and not mercurous sulfide, as shown by the following:<sup>5</sup>



**3. Mercurous Hydroxide,  $\text{HgOH}$ , and Mercurous Oxide,  $\text{Hg}_2\text{O}$ .**—Add a dilute solution of  $\text{NaOH}$  to a test solution of  $\text{Hg}_2(\text{NO}_3)_2$ . What is the result? Let stand in the sunlight or warm, and describe what change takes place. Can  $\text{NH}_4\text{OH}$  be used in place of  $\text{NaOH}$ ?

**4. Additional Precipitates of Mercurous-ion.**—Mercurous chromate,  $\text{Hg}_2\text{CrO}_4$ , red; mercurous iodide,  $\text{Hg}_2\text{I}_2$ , green or may be gray or yellow according to the concentration of the solutions used.

**5. Precipitation of Metallic Mercury,  $\text{Hg}^\circ$ .**—Place a clean strip of copper in a solution of mercurous nitrate. Describe the result and give an explanation.

### EXERCISES

1. Your test solution of  $\text{Hg}_2(\text{NO}_3)_2$  is acid. Obtain a small crystal of the salt from the supply shelf and add water to it. Warm if necessary. Explain now why your test solution is acid. How would you prepare the test solution?

2. If  $\text{Hg}_2\text{Cl}_2$  is changed to  $\text{HgNH}_2\text{Cl}$  and  $\text{Hg}$  by the addition of  $\text{NH}_4\text{OH}$ , show the oxidation-reduction change by either the valence-change or the electron-change method.

3. How would you account for the great instability of  $\text{Hg}_2\text{S}$  even in the presence of the reducing agent  $\text{H}_2\text{S}$ ?

4. How does the basic forming character of mercurous mercury compare with that of silver?

### LEAD-ION, $\text{Pb}^{++}$ (COLORLESS)

**1. Lead Chloride,  $\text{PbCl}_2$ .**—Precipitate  $\text{PbCl}_2$  from a test solution of  $\text{Pb}(\text{NO}_3)_2$  by the addition of  $\text{HCl}$ . Write the equation for the reaction and give the physical appearance of the precipitate. Decant, and wash the precipitate once with cold water. Pass  $\text{H}_2\text{S}$  through the wash water. The black precipitate is  $\text{PbS}$ . What does this show about the solubility of  $\text{PbCl}_2$  in cold water? Add 5 cc. of water to the precipitate and heat to boiling. What

<sup>5</sup>  $\text{Hg}_2\text{S}$  is unstable above  $-10^\circ$ , and consequently is not formed permanently at room temperature.

is shown about the solubility in hot water? Suggest a simple method of separating  $\text{PbCl}_2$  from  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$ . Will the lead be taken out entirely by the addition of Group I reagent? Concentrate the solution of  $\text{PbCl}_2$  to about 4 cc. Cool and note the results. If lead is to be removed as a chloride in Group I, what care must be taken in controlling the temperature and the concentration? Transfer a portion of the precipitate to another test tube and add, dropwise, concentrated  $\text{HCl}$ . Compounds of the type of  $\text{PbCl}_2 \cdot 2\text{HCl}$  (sometimes written  $\text{H}_2\text{PbCl}_4$ ) are formed. Explain the reaction. What caution must be exercised in precipitating Group I with  $\text{HCl}$ ? To another portion of the precipitate of  $\text{PbCl}_2$  add  $\text{NH}_4\text{OH}$ . A white substance,  $\text{Pb}(\text{OH})\text{Cl}$  (a basic salt), results. This precipitate is very insoluble. How could you prove that  $\text{PbCl}_2$  is no longer present. Have you noticed any decomposition of  $\text{PbCl}_2$  in the light as you have been working?

**2. Lead Chromate,  $\text{PbCrO}_4$ .**—Take some of the lead chloride solution, or the original test solution and add a few drops of potassium chromate,  $\text{K}_2\text{CrO}_4$ . The yellow precipitate is  $\text{PbCrO}_4$ . Write the equation. See if its solubility in hot water is greatly increased. To show how the physical appearance of a precipitate may be changed by conditions of precipitation, take 2 cc. of a saturated solution of  $\text{PbCl}_2$  and add 5 drops of a saturated solution of  $\text{K}_2\text{CrO}_4$ . How do the two precipitates compare? See Plate I, *D* and *E*.

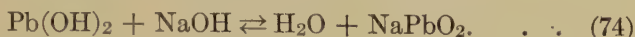
**3. Lead Sulfate,  $\text{PbSO}_4$ .**—Add a few drops of dilute  $\text{H}_2\text{SO}_4$  to a soluble lead-salt solution. Describe the physical appearance of the precipitate. Is the compactness of  $\text{PbSO}_4$  indicated by its rate of settling? Is the solubility of the salt increased in hot water or in an excess of dilute  $\text{H}_2\text{SO}_4$ ?  $\text{PbSO}_4$  is somewhat soluble in concentrated mineral acids because of the formation of the  $\text{HSO}_4^-$  ion. Compare the volumes of different precipitates containing the same amounts of lead by precipitating  $\text{PbCrO}_4$  from 5 cc. of a test solution of  $\text{Pb}(\text{NO}_3)_2$ , and  $\text{PbSO}_4$  from an equal volume of the same test solution.

Which precipitate would give the better test in a very dilute solution containing lead? Dissolve, as far as possible, some  $\text{PbSO}_4$  in strong acetic acid containing some solid ammonium acetate. Use an evaporating dish and warm gently. Decant a few drops of the solution from time to time and test with  $\text{K}_2\text{CrO}_4$  to determine how rapidly the  $\text{PbSO}_4$  is going into solution.



**4. Lead Sulfide, PbS.**—Place in three test tubes equal portions of a test solution of  $\text{Pb}(\text{NO}_3)_2$ . Make the first weakly acid, the second approximately neutral and the third weakly basic. The formation of precipitates during the adjustment of the solutions will not interfere with the results, so leave them in the test tubes. Now pass  $\text{H}_2\text{S}$  slowly through the solutions. Explain the results. Try to precipitate PbS in the presence of much HCl. Test the solubility of the sulfide in  $6n \text{ HNO}_3$ .

**5. Lead Hydroxide,  $\text{Pb}(\text{OH})_2$ .**—Precipitate  $\text{Pb}(\text{OH})_2$  from a test solution by the addition of dilute NaOH. Now add concentrated NaOH and warm. The precipitate dissolves because of the formation of a plumbite radical,  $\text{PbO}_2^-$ :



The structural change is shown in:



Prepare another portion of  $\text{Pb}(\text{OH})_2$  in which  $\text{NH}_4\text{OH}$  is used as the precipitating agent. Is the precipitate soluble in an excess of  $\text{NH}_4\text{OH}$ ?

**6. Additional Precipitates of Lead-ion.**—Lead iodide,  $\text{PbI}_2$ , yellow; lead cyanide  $\text{Pb}(\text{CN})_2$ , white; lead phosphate,  $\text{Pb}_3(\text{PO}_4)_2$ , white.

**7. Precipitation of Metallic Lead,  $\text{Pb}^\circ$ .**—What are the possibilities of precipitating lead from solutions by the addition of other metals?

## EXERCISES

1. A mixed precipitate of  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$  is contaminated with  $\text{PbCl}_2$ . When  $\text{NH}_4\text{OH}$  is added, can you see any difficulty that might arise from the presence of the  $\text{PbCl}_2$ ?

2. Write the ionization constant for  $\text{PbSO}_4$  and explain how it may have a slight solubility in concentrated HCl.

3. Show by solubility relationships how lead hydroxide can gradually change to lead sulfide by passing  $\text{H}_2\text{S}$  through a solution containing the precipitate of  $\text{Pb}(\text{OH})_2$ .

4. Since a plumbite results when NaOH is added to a precipitate of

$\text{Pb}(\text{OH})_2$ , but not when  $\text{NH}_4\text{OH}$  is used, what theoretical principles can be here applied? If the precipitate had also dissolved in  $\text{NH}_4\text{OH}$ , what would you have concluded?

#### SUMMARY OF REACTIONS OF THE IONS IN GROUP I THAT ARE OF IMPORTANCE IN ANALYTICAL PROCEDURE

In selecting a group precipitating reagent there is more to be considered than the mere precipitation of the group. The precipitates containing the group radicals must be subdivided in such a way that the radicals can be separated and identified. A group precipitate that cannot be satisfactorily dissolved, or when dissolved is in a solution that will not lend itself to further subdivision, is practically worthless.

There are two general methods of analyzing a group precipitate: first, the entire group may be dissolved, and then a certain portion reprecipitated; or second, a solvent which only dissolves a part of the original precipitate may be added.

In precipitating Group I, the chlorides of the radicals are found to have the desired group characteristics just described, and we shall use  $\text{HCl}$  as the precipitating reagent. We have determined that, in order to retain most of the lead in this group, the solution cannot be too dilute and must be kept cold. The reagent is not to be added in large excess, because of the possibility of complex-ion formation.

After the group precipitate has been filtered and washed, the lead chloride can be removed from the chlorides of silver and mercurous mercury by dissolving in hot water. Confirmatory tests for  $\text{Pb}^{++}$  can be made with either  $\text{H}_2\text{SO}_4$  or  $\text{K}_2\text{CrO}_4$ .

By pouring  $\text{NH}_4\text{OH}$  over the residue consisting of  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$ , the silver salt is dissolved by the formation of the complex ion  $\text{Ag}(\text{NH}_3)_2^+$ . Identification of  $\text{Ag}^+$  is made by acidifying the filtrate. The black residue containing  $\text{Hg}$  and  $\text{HgNH}_2\text{Cl}$  identifies  $\text{Hg}_2^{++}$ . This test, however, can be confirmed by dissolving the black residue in aqua regia and then adding  $\text{SnCl}_2$  solution after the excess acid has been boiled out and the solution diluted with water.

PROCEDURE FOR THE ANALYSIS OF A PRACTICE SOLUTION CONTAINING GROUP I<sup>6</sup>

**Precipitation of Group I.**—The practice solution contains 5 cc. each of test solutions of  $\text{Ag}^+$ ,  $\text{Hg}_2^{++}$  and  $\text{Pb}^{++}$ .<sup>a</sup> (A detailed explanation of references is given in a set of notes which immediately follows this procedure.) Place the solution in a 200-cc. flask, dilute with 10 cc. of cold distilled water and precipitate slowly with  $3n$   $\text{HCl}$  in slight excess. Allow the precipitate to settle between additions of acid so that it can be determined when the addition of acid produces no further precipitation.<sup>b</sup> Filter immediately and wash once with 2 cc. of cold water to which have been added 3 drops of dilute  $\text{HCl}$ . Wash a second time with the same amount of cold water.<sup>c</sup> The filtrate and washings can be discarded unless there is a subsequent group present. The precipitate consists of  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$  and  $\text{PbCl}_2$ .

**Separation and Identification of Lead.**—Heat 8 cc. of water nearly to boiling and pour over the precipitate. Reheat the solution that has passed through, and again pour it on the precipitate. Finally wash the precipitate with 2 cc. of hot water and combine filtrate and washings. To test for lead in the solution, divide it into two parts. To the first add a few drops of dilute  $\text{H}_2\text{SO}_4$ , giving the white crystalline precipitate of  $\text{PbSO}_4$ . To the second part<sup>d</sup>, add 2 cc.  $\text{HNO}_3$ <sup>e</sup>, then 2 cc.  $3n$   $\text{K}_2\text{CrO}_4$ . A yellow, flocculent precipitate of  $\text{PbCrO}_4$  results. Both are final tests for lead.

**Identification of Mercury.**—Pour 5 cc.  $6n$   $\text{NH}_4\text{OH}$  over the residue on the filter and reserve the filtrate for the identification of silver. A gray or black precipitate indicates a mixture of  $\text{HgNH}_2\text{Cl}$  and  $\text{Hg}$  and is the final test for mercury.

**Identification of Silver.**—The filtrate<sup>f</sup> from the  $\text{NH}_4\text{OH}$  treatment is made acid with  $\text{HNO}_3$ , and a white precipitate of  $\text{AgCl}$  indicates the presence of silver.<sup>g</sup>

<sup>6</sup> When there are succeeding groups present, the initial treatment of the solution in the analysis of each group is occasionally modified. For example, where Group II is present as well as Group I, antimony, bismuth and tin may be precipitated by hydrolysis when the original solution is diluted with water before the Group I precipitating reagent is added. These special situations will be discussed in detail when we analyze solutions containing all of the groups of cations.

## NOTES ON THE PROCEDURE FOR THE ANALYSIS OF GROUP I

a. In the analysis of unknown solutions, later on, the amount of precipitate is to be compared with that which resulted in the preliminary tests, or in the practice solution, where it is known that there are approximately 10 mg. of radical per cubic centimeter of test solution.

b. The partial solution of some of the chlorides by the formation of complexes in excess acid is possible. A maximum excess of 1 cc. of dilute acid will not seriously interfere. Find out approximately how many drops there are in 1 cc.

c. Where only a trace of lead is present, it will go to Group II, even by this careful treatment. A group precipitate must always be washed to remove subsequent groups present in solution. A failure to do this might be harmful in two ways: first, by losing some of the following groups; and second, by contaminating the precipitate under examination.

d. Where more than one test is given for a radical, it is not necessary to obtain perfect tests by all methods. Sometimes one method will work better than another. Obtain one good test and be satisfied with that.

e. Where there are succeeding groups present in a solution together with a group precipitate, it may happen that some of the radicals are retained by the group precipitate because of insufficient washing. Chromates of the alkaline earth group (Group IV) are quite insoluble, and if formed when  $K_2CrO_4$  is added to the solution would also precipitate. The presence of  $HNO_3$  allows the precipitation of  $PbCrO_4$  only, since it is more insoluble in acids.

f. A turbidity in the filtrate is probably caused by the formation of colloidal  $Pb(OH)Cl$ , as a result of the inefficient removal of  $PbCl_2$  when washing with hot water. This basic salt is soluble in  $HNO_3$ , so that it will be dissolved when the  $AgCl$  is finally precipitated. If the turbidity caused by the  $Pb(OH)Cl$  should obscure the  $AgCl$  test, it can be removed by refiltering through a double filter before adding the  $HNO_3$ .

g. If an unknown contains a large excess of  $Hg_2^{++}$  and very little  $Ag^+$ , the  $AgCl$  may not dissolve when  $NH_4OH$  is added, but will be reduced to  $Ag^0$ . This condition might be suspected if a black precipitate resulted on the filter paper, and later a slight turbidity was all that could be obtained in a test for  $Ag^+$ . Where this happens, punch a hole in the bottom of the filter paper, wash the precipitate down into an evaporating dish with the least amount of water possible, digest in aqua regia, cool, dilute and filter through a fresh piece of paper. The  $AgCl$  should now be alone on the paper, and can be tested for by washing first with  $NH_4OH$  and then acidifying the filtrate with 3*N*  $HNO_3$ . The solution is diluted after digesting with aqua regia and before filtering, because  $AgCl$  is somewhat soluble in concentrated  $HCl$ .

If an additional mercury test is desired, first boil off the excess chlorine from the  $AgCl$  filtrate, and then add, dropwise, a solution of  $SnCl_2$ . Since mercury is present as  $HgCl_2$ , it will first give a white precipitate of  $HgCl$  and finally the blue-black of  $Hg^0$ .



## OPTIONAL TESTS IN THE ANALYSIS OF GROUP I

Group I is so small that there are not many variations in the methods of analysis. One variation, however, consists in precipitating the group and filtering after boiling. All of the lead will, therefore, be carried on to Group II. This procedure is questionable, because in the second group the lead is supposed to be removed in the first part of sub-division A. If any lead passes into the latter part of this sub-division, it practically destroys one of the tests, that for cadmium. By removing as much of the lead as possible in Group I, it is only necessary to take care of a small amount in Group II.

In another procedure the HCl group is not removed first, but after acidifying the original solution  $H_2S$  is immediately passed through and Groups I and II are combined. The resulting group thereby becomes very large and increasingly difficult to handle.

The reagent  $NH_4Cl$  is sometimes used to precipitate the group. It avoids the danger of complex-ion formation due to the addition of a large excess of HCl.

A third test for lead can be made by adding a solution of KI to that of  $PbCl_2$ , giving a yellow precipitate of  $PbI_2$ . It offers no advantage over the  $PbCrO_4$ . About the only difficulty encountered in the use of  $PbCrO_4$  is that it sometimes comes out in colloidal suspension if  $K_2CrO_4$  is added rapidly and in too large an amount.

In separating  $HgNH_2Cl$  and Hg from Ag, where there is a large excess of mercury, HCl and saturated bromine water can be used instead of the aqua regia. In this treatment it is not necessary to remove the precipitate from the paper, as the solutions can be poured over the solids one or more times. The mercury is changed to soluble  $HgBr_2$ , the silver to insoluble  $AgBr$  and the  $HgNH_2Cl$  to soluble  $HgCl_2$ .

Absolute alcohol is sometimes used to decrease the solubility of certain precipitates that have a small solubility in water or weak acids. On the addition of the alcohol, the insoluble salt has a tendency to appear as a turbidity. If the precipitate of  $PbSO_4$ , for example, is unsatisfactory, a few drops of concentrated alcohol may give better results. To the use of alcohol, however, to promote the formation of precipitates there are two objections: first, when it is very concentrated there is a tendency to precipitate the fairly soluble salts as well as the sparingly soluble ones; and second, when it is exposed to the air it gradually absorbs water so that it will eventually retard precipitation instead of promoting it.



## PROCEDURE SHEET I

## ANALYSIS OF GROUP I

Final tests are underscored twice

Fifteen cubic centimeters of practice solution contain approximately 50 mg. each of  $\text{Ag}^+$ ,  $\text{Hg}_2^{++}$  and  $\text{Pb}^{++}$ . Add 10 cc. distilled water, ppt. with  $3n$   $\text{HCl}$  in slight excess, filter, wash with cold water containing a few drops of  $\text{HCl}$ , then with cold water.

Precipitate: <u><math>\text{Hg}_2\text{Cl}_2</math></u> , <u><math>\text{AgCl}</math></u> , <u><math>\text{PbCl}_2</math></u> . Extract with hot water.		Filtrate:
Residue: <u><math>\text{Hg}_2\text{Cl}_2</math></u> , <u><math>\text{AgCl}</math></u> . Extract with $\text{NH}_4\text{OH}$ .		Traces of $\text{PbCl}_2$ , and subsequent groups when present.
Residue:	Filtrate:	
<u><math>\text{HgNH}_2\text{Cl}</math></u> , <u><math>\text{Hg}</math></u>	$\text{Ag}(\text{NH}_3)_2\text{OH}$ .	
white      bluish-black	Add $6n$ $\text{HNO}_3$	(1) Adding $\text{K}_2\text{CrO}_4$
mixture is gray	until acid, giving white ppt. of <u><u><math>\text{AgCl}</math></u></u> .	to one-half filtrate made acid with a few drops of $\text{HNO}_3$ , giving yellow ppt. of <u><u><math>\text{PbCrO}_4</math></u></u> .
Can be identified further by dissolving in aqua regia, boiling, diluting, filtering and adding dropwise $\text{SnCl}_2$ .		(2) Adding $\text{H}_2\text{SO}_4$ to other half, giving white ppt. of <u><u><math>\text{PbSO}_4</math></u></u> .
<u><u><math>\text{HgCl}</math></u></u> and <u><u><math>\text{Hg}</math></u></u>		
white      bluish-black		
mixture is gray		

## CHAPTER IV

### GROUP II.—THE HYDROGEN SULFIDE OR ACID SULFIDE GROUP

MERCURY(IC),	Hg; at. wt. 200.6; Hg <sup>++</sup>
LEAD,	Pb; at. wt. 207.2; Pb <sup>++</sup>
BISMUTH,	Bi; at. wt. 209.0; Bi <sup>+3</sup>
COPPER,	Cu; at. wt. 63.57; Cu <sup>+</sup> , Cu <sup>++</sup>
CADMIUM,	Cd; at. wt. 112.41; Cd <sup>++</sup>
ARSENIC,	As; at. wt. 74.96; As <sup>+3</sup> , As <sup>+5</sup>
ANTIMONY,	Sb; at. wt. 121.77; Sb <sup>+3</sup> , Sb <sup>+5</sup>
TIN,	Sn; at. wt. 118.70; Sn <sup>++</sup> , Sn <sup>+4</sup>

This group consists of cations that were not precipitated in Group I and whose sulfides are insoluble in 0.3*n* HCl within a limited period of time.

#### PRELIMINARY TESTS

##### MERCURIC-ION, Hg<sup>++</sup> (COLORLESS)

**1. Mercuric Sulfide, HgS.**—Add 5 cc. 6*n* HCl to 5 cc. test solution of HgCl<sub>2</sub>, dilute with 100 cc. water and precipitate in a flask with H<sub>2</sub>S. Describe the precipitate and write the equation for the reaction. Did the precipitate change color during precipitation? It sometimes happens during the precipitation of HgS that intermediate compounds are formed which consist of various proportions of the mercuric salt in solution and HgS. For example, where the soluble salt is HgCl<sub>2</sub>, the intermediate series may consist of HgCl<sub>2</sub>·HgS; HgCl<sub>2</sub>·2HgS; etc. When H<sub>2</sub>S is in large excess in the flask, the end product is black HgS.

When Group II is being precipitated by H<sub>2</sub>S, the formation of intermediate compounds of mercuric sulfide may be misleading, because their colors range from a yellowish-white, through the light yellow which is characteristic of arsenic sulfide then through orange-yellow of cadmium sulfide and the orange-red of antimony

sulfide, finally developing the black of  $\text{HgS}$ . The intermediate compounds are possible when test solutions of any soluble mercuric salt are used. They are not restricted, as some believe, to test solutions of  $\text{HgCl}_2$ .

To form the intermediate double compounds of mercury, take 5 cc. test solution of  $\text{Hg}(\text{NO}_3)_2$ , dilute with 5 cc. water, then add in 1-cc. portions, water that has been saturated with  $\text{H}_2\text{S}$ . Shake between additions and the color series will be formed without any difficulty.

Take the black precipitate of  $\text{HgS}$ , filter and wash once with hot water. Test small portions of the precipitate in test tubes with  $6n$   $\text{HNO}_3$  and  $16n$   $\text{HNO}_3$ . Carefully warm the  $16n$   $\text{HNO}_3$  if no change occurs otherwise. A white precipitate in the concentrated acid is  $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgS}$ . Test the solubility of some  $\text{HgS}$  in an evaporating dish with aqua regia, and warm if necessary to complete solution. The addition of a few small crystals of  $\text{KClO}_3$  will often assist in hastening solution.<sup>1</sup> Should concentrated  $\text{HCl}$  dissolve  $\text{HgS}$ ? Try the solubility of  $\text{HgS}$  in solutions of  $\text{KOH}$ ,  $\text{NH}_4\text{OH}$ ,  $(\text{NH}_4)_2\text{S}_x$  (ammonium polysulfide) and  $\text{Na}_2\text{S}_x$ . Summarize your solubility tests. Where there is only a slight solubility it cannot be determined by a casual inspection and a test involving a characteristic chemical reaction should be made. It is necessary to know if there is a slight solubility of  $\text{HgS}$  in the polysulfides as this fact will be made use of in subsequent analysis. Devise a method at this point which will enable you to determine if limited solution has occurred. This is an excellent opportunity to test your understanding of some of the principles of analytical chemistry.

Heat the liquid resulting from the solution of  $\text{HgS}$  in aqua regia until the excess chlorine is driven off. How will you determine this? Cool, dilute and filter. Why dilute? Why filter? Is there any objection to excessive dilution? Add, dropwise, to the clear filtrate, a solution of  $\text{SnCl}_2$ . Where has this test been used before? For what radicals can the test be employed?

**2. Mercuric Hydroxide,  $\text{Hg}(\text{OH})_2$ , and Mercuric Oxide,  $\text{HgO}$ .**—Add to a solution of  $\text{KOH}$  or  $\text{NaOH}$  3 cc. of a test solution of  $\text{HgCl}_2$ . A basic salt may appear at first. Upon a further addi-

<sup>1</sup> Do not discard the resulting solutions until you are through with all of the tests of the particular radical. The solutions will frequently be used in later experiments.

tion of reagent this changes into yellow  $\text{HgO}$ . Why do we not obtain the hydroxide? Is the oxide soluble in an excess of reagent? Repeat the experiment, using  $\text{NH}_4\text{OH}$  in place of  $\text{NaOH}$ . The white precipitate is  $\text{HgNH}_2\text{Cl}$ . Compare this reaction with a previous one involving  $\text{Hg}_2\text{Cl}_2$ .

**3. Additional Precipitates of Mercuric-ion.**—Mercuric iodide,  $\text{HgI}_2$ , may be yellow at first but quickly changes to red and is soluble in excess of reagent; mercuric chromate,  $\text{HgCrO}_4$ , may be yellow at first but quickly changes to brown and cannot be precipitated from a solution of  $\text{HgCl}_2$ . An odd solubility is shown by white  $\text{Hg}(\text{CN})_2$  which readily dissolves in water. It is the only cyanide of a heavy metal that is not a precipitate in water. Do not guess at solubilities.

**4. The Precipitation of Metallic Mercury,  $\text{Hg}^\circ$ ,** can readily be accomplished in mercuric solutions by introducing clean strips of Cu, Zn, Fe, etc.

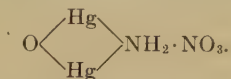
## EXERCISES

1. The white intermediate precipitate which may be formed when  $\text{H}_2\text{S}$  is passed into  $\text{HgCl}_2$  results from the reaction of  $3\text{HgCl}_2$  and  $2\text{H}_2\text{S}$ . Write an equation for the reaction. Show in a second equation how the intermediate compound is finally changed to  $\text{HgS}$ .

2. Write the equation for the solution of  $\text{HgS}$  in aqua regia.

3. In adding solutions of  $\text{HgCl}_2$  and  $\text{SnCl}_2$  does it make any difference which one is added dropwise to the other? Work this question out on a theoretical basis and then test it experimentally. What is the best method of performing the test?

4. When  $\text{NH}_4\text{OH}$  reacts with a test solution of  $\text{Hg}(\text{NO}_3)_2$ , oxy-di-mercuriammonium nitrate results. Its structural formula is:



Write the rest of the reaction. This reaction is given because you may have started with a test solution of  $\text{Hg}(\text{NO}_3)_2$  instead of  $\text{HgCl}_2$ ; consequently you may have been curious to know what it was that resulted when the reagent  $\text{NH}_4\text{OH}$  was used. Perhaps you inferred that it was  $\text{HgNH}_2\text{NO}_3$ . This is a good illustration of the fact that the compounds which result from reactions are not determined by mathematical processes.

5. Explain why  $\text{HgCrO}_4$  cannot be precipitated from a solution of  $\text{HgCl}_2$ .

LEAD-ION,  $Pb^{++}$  (COLORLESS)

Some of the preliminary tests with lead-ion were considered in Group I. However, since it may not be completely removed as  $PbCl_2$  at that point in analysis, provision must be made for its complete removal in Group II. Review the tests involving  $PbS$  and  $PbSO_4$ . Note especially that where the acidity is too great the precipitate will not form. Sometimes, as with mercuric chloride, an intermediate precipitate results which is dark red and probably  $PbCl_2 \cdot PbS$  or  $PbCl_2 \cdot 2PbS$ . Test the solubility of  $PbS$  in  $16n$   $HNO_3$ . The result can be interpreted by inspecting the following equation:



Where does the  $SO_4^{=}$  come from? What other precipitate may be present besides the  $PbSO_4$ ? Can you dissolve  $PbS$  with  $HCl$ ? Test the solubility of  $PbS$  in  $(NH_4)_2S_x$  and  $Na_2S_x$ . How do  $PbS$  and  $HgS$  compare in this respect?

Precipitate some  $PbSO_4$  from a test solution of  $Pb(NO_3)_2$  as you did in Group I. Filter through two thicknesses of paper and pass  $H_2S$  through the clear filtrate. What will you conclude? In systematic analysis it is very necessary to remove traces of lead completely. Precipitate more  $PbSO_4$  in an evaporating dish, add 2 cc. concentrated  $H_2SO_4$  in excess of that necessary for complete precipitation, and evaporate under the hood until white fumes of  $SO_3$  appear. However, do not reduce the volume to less than one-third. Cool, dilute carefully by pouring into an equal volume of water and permit the precipitate of  $PbSO_4$  to settle. Decant off most of the liquid. Why not dilute by pouring the other way? What other acid is present besides  $H_2SO_4$ ? The presence of this other acid is believed to promote the formation of the more soluble  $Pb(HSO_4)_2$ . How does evaporation remove the second acid? Note the compactness and granular character of the  $PbSO_4$  formed in this experiment and the fact that it is difficult to see against the white background of the evaporating dish. Does the precipitate wash well by decantation? Why? What is the objection to pouring the solution containing the  $PbSO_4$  on a filter paper?

Determine whether  $PbSO_4$  will precipitate in the presence of weak or concentrated acetic acid.



## EXERCISES

1. Show, by using the constants  $K_{SP}$  for  $PbS$  and  $K_{ion}$  for  $H_2S$ , why  $PbS$  cannot be precipitated from a solution that is too strongly acid.
2. If Group II is to be precipitated by  $H_2S$  in a weakly acid solution, what are the relative merits of  $HNO_3$ ,  $H_2SO_4$  and  $HCl$  for giving that acidity?
3. If  $PbSO_4$  will dissolve in a mixture of ammonium acetate and acetic acid, what can be concluded about the relative extent of ionization of  $PbSO_4$  and  $PbAc_2$ ?<sup>2</sup> What exception to a very general rule is here shown?

BISMUTH-ION,  $Bi^{+3}$  (COLORLESS)

1. **Bismuth Sulfide,  $Bi_2S_3$ .**—Add 5 cc. 6*n*  $HCl$  to 5 cc. test solution of  $Bi(NO_3)_3$ , dilute with 100 cc. water and precipitate with  $H_2S$ . If a white precipitate forms during dilution with water, add more acid to redissolve. Filter and wash with hot water. Write the equation and describe the characteristics of the precipitate. Test the solubility in cold and hot 6*n*  $HNO_3$ , cold and hot 12*n*  $HCl$ ,  $(NH_4)_2S_x$ ,  $Na_2S_x$ , and  $KCN$ .<sup>3</sup> In what respects are the solubilities of  $Bi_2S_3$  like those of  $PbS$ ?

2. **Bismuth Hydroxide,  $Bi(OH)_3$ .**—Precipitate the hydroxide  $Bi(OH)_3$  by adding  $KOH$  or  $NaOH$  to test solutions of  $Bi(NO_3)_3$ . Describe the precipitate. Is it soluble in excess of reagent? Filter and wash with hot water. Test the solubility of portions of the precipitate in 6*n*  $HCl$  and 6*n*  $HNO_3$ . Lift the filter paper out of the wet funnel and place it in a dry one. Now add to the remainder of the precipitate 10 drops 12*n*  $HCl$  and catch 2 drops of the concentrated solution of  $BiCl_3$ , coming out of the funnel stem, in a beaker of cold water. The white precipitate formed in the water is bismuth oxychloride. The equation is:



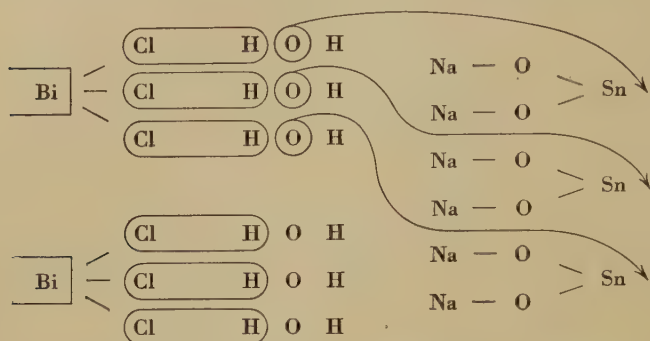
Why was a dry funnel used? What type of reaction is this? Why is the volume of acid used in dissolving the  $Bi(OH)_3$  kept small? Do you think that  $BiOCl$  is soluble in  $HCl$ ? Notice the dispersion of the white precipitate in the water upon standing. When is this test most efficient?

<sup>2</sup> In qualitative work the organic radicals are often abbreviated as acetate Ac; oxalate, Ox; Tartrate, Tr.

<sup>3</sup> Use  $KCN$  only with permission and supervision of your instructor.

Catch two more drops of  $\text{BiCl}_3$  in a test tube containing freshly prepared sodium stannite solution.<sup>4</sup>

The reaction with sodium stannite is shown graphically:



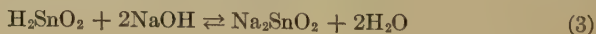
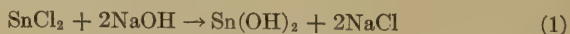
By starting with  $2\text{BiCl}_3$  and  $3\text{Na}_2\text{SnO}_2$ ,  $2\text{Bi}$  is precipitated out; the three molecules of stannite change to the same number of molecules of stannate by obtaining  $3\text{O}^-$  from  $\text{OH}^-$  ions of  $\text{H}_2\text{O}$ . The other products are  $6\text{HCl}$  and  $3\text{H}_2\text{O}$ . Write the complete equation and notice that the acidity has increased. If the sodium stannite is alkaline, what further reaction can take place?

Add  $\text{NH}_4\text{OH}$  to a test solution of  $\text{Bi}(\text{NO}_3)_3$ . A basic salt of varying composition is formed, and not a true hydroxide. After complete precipitation add an excess of  $\text{NH}_4\text{OH}$ . Does the precipitate redissolve? Is bismuth hydroxide amphoteric? Does its ion enter into complex ammonia radicals?

**3. Additional Precipitates of Bismuth-ion.**—Bismuth tri-iodide,  $\text{BiI}_3$ , black; bismuthyl dichromate,  $(\text{BiO})_2\text{Cr}_2\text{O}_7$ , orange-red; bismuthyl sulfate,  $(\text{BiO})_2\text{SO}_4$  (sometimes written  $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$ ), white; bismuth phosphate,  $\text{BiPO}_4$ , white.

**4. Metallic Bismuth,  $\text{Bi}^0$ ,** is precipitated from solutions by metals higher in the electromotive series.

<sup>4</sup> This solution must be prepared just before using. Put in a test tube 5 cc.  $m$   $\text{SnCl}_2$  (be sure it is stannous). Add, dropwise,  $\text{NaOH}$  solution until a good precipitate has been formed, and then add more until the precipitate has just about redissolved. A slight turbidity should still be present. Cool this solution before using. The reactions are:



## EXERCISES

1. In the reaction between  $\text{BiCl}_3$  and  $\text{Na}_2\text{SnO}_2$ , consider that hydrolysis takes place first, forming  $\text{Bi}(\text{OH})_3$ . Write a new equation for the reaction. The two types of reactions probably occur simultaneously.

2. In preparing sodium stannite solution, show by the equation for the proper equilibrium reaction that a slight precipitate of  $\text{Sn}(\text{OH})_2$  can be present in a weakly acid solution.

3. If the stannite solution is too strongly alkaline there is a danger of black Sn precipitating. Write the equation to show the reaction.

CUPROUS-ION,  $\text{Cu}^+$  (COLORLESS)

While the cupric compounds are of more common occurrence than the cuprous in qualitative procedure, there are a few of the latter which are worth considering.

Boil a solution of cupric chloride,  $\text{CuCl}_2$ , with  $12n$  HCl and copper turnings. The blue color should gradually decrease as  $\text{Cu}^{++}$  becomes  $\text{Cu}^+$ . The reaction develops complexes as  $\text{H}_2\text{CuCl}_3$  and  $\text{HCuCl}_2$ , which are decomposed by the addition of water. Add cold water, filter the white precipitate of  $\text{Cu}_2\text{Cl}_2$  and wash once with cold water. This precipitate of  $\text{Cu}_2\text{Cl}_2$  will be used as the source of  $\text{Cu}^+$  ions.

1. **Cuprous Hydroxide,  $\text{Cu}_2(\text{OH})_2$ , and Cuprous Oxide,  $\text{Cu}_2\text{O}$ .**—Put a few of the crystals of  $\text{Cu}_2\text{Cl}_2$  in a test tube and add water. Bring to a boil. Yellow  $\text{Cu}_2(\text{OH})_2$  will first form which will finally decompose into  $\text{Cu}_2\text{O}$ . What is the color of the oxide? Has the radical  $\text{Cu}^+$  strong metallic properties? Write an equation for the formation of  $\text{Cu}_2(\text{OH})_2$ . What is the name of the process by which  $\text{Cu}_2(\text{OH})_2$  is formed by the action of water on  $\text{Cu}_2\text{Cl}_2$ ?

2. **Cuprous Sulfide,  $\text{Cu}_2\text{S}$ .**—Put some of the crystals of  $\text{Cu}_2\text{Cl}_2$  in 20 cc. of water in a test tube, add 1 cc.  $6n$  HCl and bubble  $\text{H}_2\text{S}$  through the solution. The precipitate is a mixture of black  $\text{Cu}_2\text{S}$  and black  $\text{CuS}$ .

3. By setting aside the remainder of the  $\text{Cu}_2\text{Cl}_2$  crystals some interesting decomposition changes can be noticed. The change in color is due to the formation of colloidal Cu which occurs during the decomposition of  $\text{Cu}_2\text{Cl}_2$  into cupric compounds. The adsorbed metallic particles as they gather into larger masses change in color from violet to black. Other reactions involving cuprous-ion will be considered together with cupric-ion.

## EXERCISES

1. Why is it possible to precipitate  $\text{Cu}_2\text{S}$  and  $\text{CuS}$  from a suspension of  $\text{Cu}_2\text{Cl}_2$ ?
2. If  $\text{H}_2\text{S}$  is a reducing agent, how do you account for the presence of  $\text{CuS}$  when a cuprous salt is the one which supplies both ions?
3. When  $\text{CuS}$  is precipitated from a solution of  $\text{CuCl}_2$ , there is frequently a small contamination of  $\text{Cu}_2\text{S}$ . How do you account for this?
4. Write an equation to show the decomposition of cuprous chloride into cupric chloride.

CUPRIC-ION,  $\text{Cu}^{++}$  (BLUE)

The color of cupric-ion is variously described as blue, green, pale blue and bluish-green (see Plate I, *G*). A solution of the ion itself is undoubtedly blue, but since there may also be un-ionized molecules present which have color characteristics, the color of the solution is the net result of the two.<sup>5</sup> Undissociated molecules of  $\text{CuCl}_2$  and brown  $\text{CuBr}_2$  will give various blue-green combinations with blue  $\text{Cu}^{++}$ , depending upon the dilution and the corresponding degree of ionization.

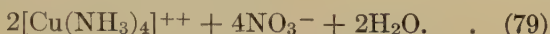
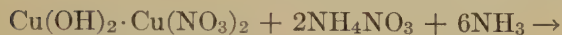
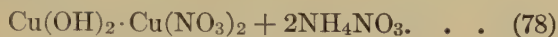
**1. Cupric Sulfide,  $\text{CuS}$ .**—Put 5 cc. test solution of  $\text{Cu}(\text{NO}_3)_2$  in a flask, add 5 cc.  $6n$   $\text{HCl}$ , dilute with 100 cc. water and precipitate with  $\text{H}_2\text{S}$ . If the black precipitate has a tendency to remain in colloidal suspension, add a little more  $\text{HCl}$  and pass  $\text{H}_2\text{S}$  through for a few minutes longer. Filter and wash with hot water. Test the solubility of the precipitate in the following reagents and tabulate your results:  $6n$   $\text{HNO}_3$ ,  $16n$   $\text{HNO}_3$ ,  $12n$   $\text{HCl}$ ,  $6n$   $\text{H}_2\text{SO}_4$ ,  $18n$   $\text{H}_2\text{SO}_4$ ,  $6n$   $\text{NaOH}$ ,  $\text{Na}_2\text{Sx}$  and  $(\text{NH}_4)_2\text{Sx}$ . If the precipitate of  $\text{CuS}$  does not completely dissolve in  $6n$   $\text{HNO}_3$  warm gently and add, dropwise, more acid. Remember the exact conditions that brought about solution in  $6n$   $\text{HNO}_3$  because you will use the method later. A little sulfur may also appear during solution. Write the equation.  $\text{KCN}$  will form a complex when added to freshly precipitated  $\text{CuS}$ . Does this necessarily mean that a solution is the result? Try the experiment. It is essential to determine whether the ammonium or the sodium polysulfide has the greater solvent action. Try to determine this experimentally.

**2. Cupric Hydroxide,  $\text{Cu}(\text{OH})_2$ , and Cupric Oxide,  $\text{CuO}$ .**—Add a few drops of  $\text{NaOH}$  or  $\text{KOH}$  to a test solution of  $\text{Cu}(\text{NO}_3)_2$ .

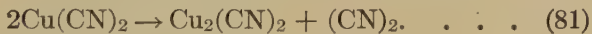
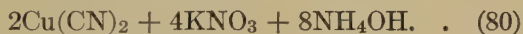
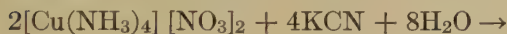
<sup>5</sup> Combinations of blue and yellow produce green color effects.

What is the color of the precipitate? Heat the solution to boiling. Describe the changes and write an equation for the result. What is a general characteristic of the hydroxides of the heavy metals? Try another portion of a test solution of  $\text{Cu}(\text{NO}_3)_2$ , but this time before precipitation with  $\text{NaOH}$  add 1 cc. of a concentrated solution of Rochelle Salt,  $\text{KNaTr}$ . What is the color of the precipitate? Now add an excess of  $\text{NaOH}$  until the precipitate redissolves. What is the color of the solution now? A complex results which is reduced to red  $\text{Cu}_2\text{O}$  when boiled with a reducing agent. Add a few drops of a solution of formaldehyde or glucose to the last solution and warm slowly. What can be tested for by the results shown in the last experiment?

Slowly add 6*n*  $\text{NH}_4\text{OH}$  to a test solution of  $\text{Cu}(\text{NO}_3)_2$ . A light blue precipitate of a basic salt will form first, and finally a clear,<sup>6</sup> deep blue solution will result (see Plate I, J). The reactions are:



The blue color of the solution is due to the presence of the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{++}$ . Divide the solution into two parts and to one portion add, dropwise, a solution of  $\text{KCN}$  until the blue color is discharged and then a few drops in excess. A new and colorless complex ion  $[\text{Cu}(\text{CN})_4]^{-3}$  has been formed. The reactions are:



These equations show how the final potassium cuprocyanide is formed. Note that copper has been reduced. Slowly pass  $\text{H}_2\text{S}$  through the two solutions and decide which complex ion is the more stable. If the difference is not apparent add a greater excess of  $\text{KCN}$  to the second portion.

<sup>6</sup> "Clear" means without a turbidity or precipitate. It does not mean colorless, as many infer.



3. **Cupric Cyanide,  $\text{Cu}(\text{CN})_2$ .**—From the reactions in “2” it is evident that a test solution of copper will give, by the gradual addition of a solution of KCN (1) a yellow precipitate of cupric cyanide which is (2) decomposed, while a white precipitate of cuprous cyanide is formed. This in turn, where the KCN is in excess, (3) dissolves, forming the complex  $[\text{Cu}(\text{CN})_4]^{-3}$ .

4. **Cupric Ferrocyanide,  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ .**—Add a few drops of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  to a test solution of copper-ion. Describe the precipitate and write the equation for its formation. Test the solubility in 6*n* nitric acid, in 6*n* acetic acid and in ammonia.

5. **Precipitation of Metallic Copper,  $\text{Cu}^0$ ,** is readily accomplished by the introduction of clean strips of metals higher in the electromotive series into copper solutions. Al, Zn and Fe are commonly used. How is copper placed in the electromotive series in relation to hydrogen?

6. **Flame Test.**—Copper salts give a characteristic bluish-green flame (see Plate IV, *F*). Also see introduction to the alkaline earth group of metals, Group IV, for a description of the method to be used in making flame tests.

7. **Borax Bead Tests** for copper give a greenish-blue bead in the oxidizing flame and a dark brown bead, tending to opaqueness, in the reducing flame (see Plate VI, *I* and *J*).

### EXERCISES

1. If  $\text{H}_2\text{S}$  will not precipitate  $\text{CuS}$  from a clear solution containing  $\text{K}_3[\text{Cu}(\text{CN})_4]$  and KCN in excess, what can be inferred about the value of  $K_{\text{Instability}}$  for the complex ion?

2. Write the instability ratio for the complex ion in “1” and show what effect upon  $[\text{Cu}^{++}]$  a decrease in the excess of KCN will have.

3. Explain why  $\text{Cu}_2\text{S}$  is more likely to be precipitated than  $\text{CuS}$  from copper cyanide complexes.

4. If  $\text{Cu}(\text{OH})_2$  will redissolve in a large excess of  $\text{NaOH}$ , what property is shown? Write the two ionization equilibria and show how the solution of  $\text{Cu}(\text{OH})_2$  is brought about by the addition of an excess of  $\text{NaOH}$ .

5. Explain how cupric ferrocyanide dissolves in  $\text{NH}_4\text{OH}$ .

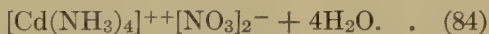
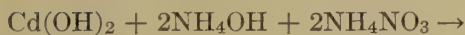
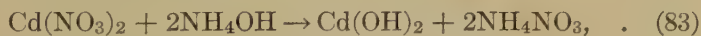
### CADMIUM-ION, $\text{Cd}^{++}$ (COLORLESS)

The tests with cadmium-ion are quite analogous to those of copper-ion, and reaction differences must be selected for the separation and identification of the one in the presence of the other.

1. **Cadmium Sulfide,  $\text{CdS}$ .**—Place 5 cc. test solution of

$\text{Cd}(\text{NO}_3)_2$  in a flask together with 5 cc. 6*n* HCl, dilute with 100 cc. water and precipitate with  $\text{H}_2\text{S}$ . If the precipitate does not settle out leaving a clear supernatant liquid, add a few more drops of acid and reprecipitate for two minutes. If the solution is still turbid, heat to boiling and allow to settle. Describe the precipitate and see Plate I, *D* and *E*, for a color comparison. Refer to this plate later when in doubt of color identification of CdS. Take another 5 cc. test solution of  $\text{Cd}(\text{NO}_3)_2$  and this time start with a dilution of 25 cc. water but with no acid. Precipitate very slowly with  $\text{H}_2\text{S}$ . Try to filter the precipitate. You may have had the conditions in these tests just right for the formation of intermediate precipitates ranging from a very light yellow to that usually described as orange or orange-red (see *J* of Plate II). The best precipitating conditions are from a hot dilute solution of moderate acidity. What is the danger in having the solution too acid? Test the solubility of CdS in 6*n*  $\text{HNO}_3$ , 16*n*  $\text{HNO}_3$ , 6*n*  $\text{H}_2\text{SO}_4$ , 6*n* NaOH,  $\text{Na}_2\text{S}_x$  and  $(\text{NH}_4)_2\text{S}_x$ . Compare the results with those obtained with CuS. In which solvents do CuS and CdS dissolve to about the same extent? In which is there a marked difference? KCN will not dissolve CdS. How does this compare with the action on CuS? We shall prepare later a complex ion containing Cd, but note here that it cannot be obtained by dissolving CdS in KCN.

**2. Cadmium Hydroxide,  $\text{Cd}(\text{OH})_2$ .**—Add KOH or NaOH to test solutions of  $\text{Cd}(\text{NO}_3)_2$ . Describe the precipitate and see whether it is soluble in an excess of reagent. Is the hydroxide unstable? Compare with cupric-ion reactions. Slowly add dilute  $\text{NH}_4\text{OH}$  to a test solution of  $\text{Cd}(\text{NO}_3)_2$ , and, when a precipitate has formed, add concentrated  $\text{NH}_4\text{OH}$  in excess. What is the result? The equations are:



Has the solution containing the complex cadmium-ion any color? Compare with copper.

Divide the solution into two parts. Pass  $\text{H}_2\text{S}$  through the first. Result? Add a few drops of KCN to the second portion, which gives the molecule  $\text{K}_2[\text{Cd}(\text{CN})_4]$ . Now pass in  $\text{H}_2\text{S}$ .

Result? Suggest a method for determining cadmium in the presence of copper.

**3. Cadmium Cyanide,  $\text{Cd}(\text{CN})_2$ .**—Slowly add a solution of KCN to a test solution of  $\text{Cd}(\text{NO}_3)_2$  until a good precipitate is formed. Describe the precipitate and write the equation for the reaction. Add KCN in excess until solution is complete. Write the equation.

**4. Cadmium Ferrocyanide,  $\text{Cd}_2 [\text{Fe}(\text{CN})_6]$ .**—Add a few drops of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  to a test solution of  $\text{Cd}(\text{NO}_3)_2$ . Result? Test the solubility of the precipitate in acetic acid and in 6*N* HCl. Could the ferrocyanide test be used to detect cadmium in the presence of copper?

### EXERCISES

1. Refer to the solubility table and decide whether the degree of acidity that will give the most compact precipitate of CdS will be the most suitable condition for the precipitation of the sulfides of the other members of Group II so far studied. In the precipitation of an entire group it is sometimes necessary to make compromises so that the maximum amount of group precipitate, and not that of one member, is obtained.

2. Discuss the amphoterism of  $\text{Cd}(\text{OH})_2$ . How does the basic strength of  $\text{Cd}(\text{OH})_2$  compare with that of  $\text{Cu}(\text{OH})_2$ ? Support your answer with experimental data.

3. Explain in detail the principle involved in determining cadmium in the presence of copper where both are first in solution as the complex ammonia ions to which later KCN is added in excess and then  $\text{H}_2\text{S}$  passed through.

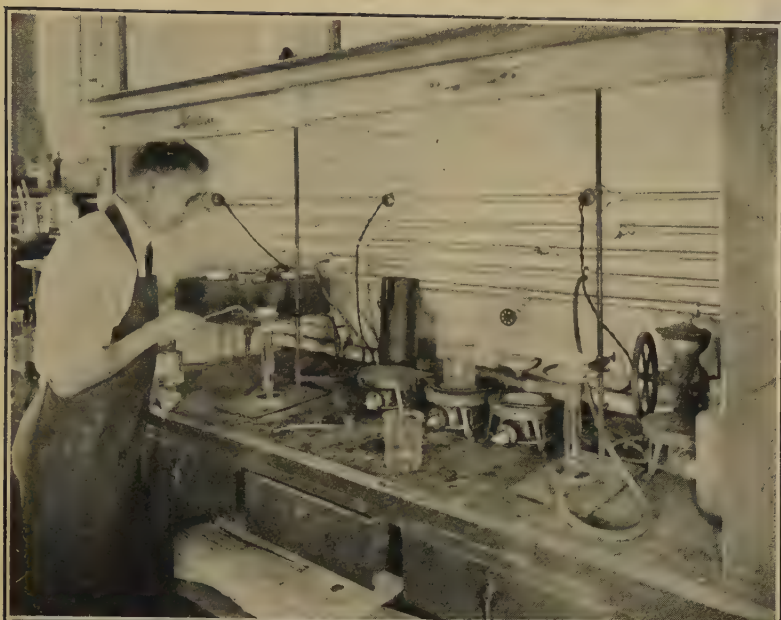
4. Write the necessary equations to show the transformation of  $[\text{Cd}(\text{NH}_3)_4][\text{NO}_3]_2$  into  $\text{K}_2[\text{Cd}(\text{CN})_4]$ .

5. Does KCN reduce the cadmium valence in the cadmium cyanide complex as it does with copper in the copper cyanide complex. Does this bring out a comparison of the metallic properties of Cd and Cu?

### ARSENIOUS-ION, $\text{As}^{+3}$ (COLORLESS)

Arsenic has two valences, +3 and +5. The corresponding oxides,  $\text{As}_2\text{O}_3$  and  $\text{As}_2\text{O}_5$ , are both amphoteric so that there are in reality four series of salts and not two. We have found that in amphoteric hydroxides either the acid or base type of ionization usually predominates and that the acid ionization is promoted as the valence is increased. Even in  $\text{As}(\text{OH})_3$  the acid properties predominate so that arsenic in both valence forms is essentially an acid-forming element.

Another factor that determines the  $[\text{H}^+]$  or  $[\text{OH}^-]$  resulting



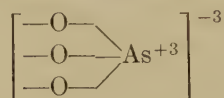
*Above.*—Research laboratory of the Bakelite Corporation, New York City.

*Below.*—Process control laboratory of the Commercial Solvents Corporation, Terre Haute, Ind. It is in control laboratories that a careful check is maintained upon manufacturing processes.



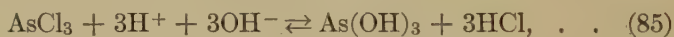
from the ionization of an amphoteric substance is its solubility. Thus,  $\text{As}_2\text{O}_3$  may be acidic in character, but if its solubility is very small the resulting  $[\text{H}^+]$  will be very limited. At  $20^\circ$  one gram of  $\text{As}_2\text{O}_3$  dissolves in about 75 cc. of water, and the solubility is increased by heating. Why will the  $[\text{OH}^-]$  be still smaller than the  $[\text{H}^+]$ ? If arsenious oxide is essentially acidic, what about its solubility in  $\text{HCl}$ ? How should it react with a strong base?

It is apparent that the source of trivalent arsenic, except for small concentrations, will not be the positive radical  $\text{As}^{+3}$  but the negative radical  $\text{AsO}_3^{-3}$ , the structural formula of which follows:



Test the solubility of one gram of  $\text{As}_2\text{O}_3$ , ordinary "white" arsenic, in 5 cc.  $12n$   $\text{HCl}$  and in  $6n$   $\text{NaOH}$ . Dilute both solutions with 25 cc. water, filter and slowly pass  $\text{H}_2\text{S}$  through the filtrates. Is the difference in solubility made apparent? Write equations to show the solution of  $\text{As}_2\text{O}_3$  in an acid and in a base.

The trichloride,  $\text{AsCl}_3$ , is a liquid, but when added to water reacts as shown by the equations:



How are the very weak metallic properties of arsenic here shown? (Give two proofs if possible.) How does this show that  $\text{AsCl}_3$  can remain in solution only when it is very acid? What will be the possibility of precipitating arsenious sulfide from a solution containing an arsenious salt?

**1. Arsenious Sulfide,  $\text{As}_2\text{S}_3$ .**—Take 6 cc. of a test solution of  $\text{AsCl}_3$  which has been prepared by digesting 1.3 grams of  $\text{As}_2\text{O}_3$  in 50 cc. of  $12n$   $\text{HCl}$  for several hours and then 50 cc. of water added. Divide the 6 cc. of solution into three equal parts and place in three test tubes. Add 15 cc. of water to the first and set aside for several hours. If any turbidity develops describe it and explain how it was formed. Add 10 cc. of water to the second tube and slowly pass  $\text{H}_2\text{S}$  through the solution for three minutes or until a turbidity develops. Try to filter this solution and note the color of the filtrate. Add more acid to a part of the colloidal sus-



pension and reprecipitate with  $\text{H}_2\text{S}$ . Describe the results. Also try the effect of adding neutral salts, as  $\text{KCl}$  or  $\text{BaCl}_2$ , to promote coagulation of the colloidal  $\text{As}_2\text{S}_3$ . Dilute the third tube with 10 cc. of water, add 15 drops of  $6n$   $\text{HCl}$  and precipitate with  $\text{H}_2\text{S}$ . A flocculent precipitate of  $\text{As}_2\text{S}_3$  should result. Write an equation for the reaction. Compare the color of the precipitate with Plate II, *E*.

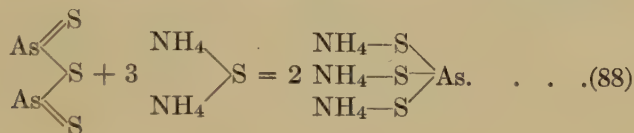
Take 5 cc. of a test solution of sodium arsenite,<sup>7</sup> add 5 cc.  $6n$   $\text{HCl}$ , dilute with 100 cc. water and slowly precipitate with  $\text{H}_2\text{S}$ . Filter and wash with hot water. Test the solubility of  $\text{As}_2\text{S}_3$  in acids,  $\text{NaOH}$ ,  $(\text{NH}_4)_2\text{S}$ ,  $(\text{NH}_4)_2\text{S}_x$  and  $\text{Na}_2\text{S}_x$ .

The solubility of  $\text{As}_2\text{S}_3$  in aqua regia is represented by:



Show the source of the 10  $\text{Cl}^-$  by an equation. What is  $\text{H}_3\text{AsO}_4$ ? If free sulfur is deposited, how are you going to tell when the yellow  $\text{As}_2\text{S}_3$  has been dissolved? The answer is very evident when you do the experiment. Carefully note all that happens during the digestion.

The reaction between  $\text{As}_2\text{S}_3$  and  $(\text{NH}_4)_2\text{S}$  is shown graphically:

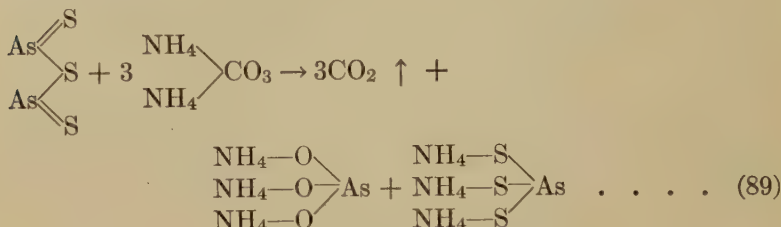


The  $(\text{NH}_4)_3\text{AsS}_3$ , ammonium sulfarsenite, is a salt of the very unstable sulfarsenious acid,  $\text{H}_3\text{AsS}_3$ , and is present, like carbonic acid,  $\text{H}_2\text{CO}_3$ , only in solutions. When liberated from its salts it immediately breaks up into  $\text{H}_2\text{S}$  and  $\text{As}_2\text{S}_3$ . The  $\text{H}_2\text{S}$  may further decompose, precipitating  $\text{S}$ . In the presence of the polysulfides the sulfarsenite is oxidized into a sulfarsenate. Write the structural formula for the sulfarsenate.

Take a solution of ammonium or sodium sulfarsenite or sulfarsenate and allow a portion to stand over night. Does it decompose spontaneously? Write the equation. To another portion add, dropwise,  $6n$   $\text{HCl}$  and warm gently between additions. Write the equation. What gas is given off? Of what may the precipitate consist?

<sup>7</sup> The alkali arsenites are the only ones soluble in water.

Dissolve some  $\text{As}_2\text{S}_3$  in a saturated solution of  $(\text{NH}_4)_2\text{CO}_3$ . Digest for several minutes if necessary, and add a few drops of water from time to time in order to keep the mass sufficiently fluid. The equation is:



After digestion, dilute with 3 cc. water and filter. The clear solution contains the soluble arsenite and sulfarsenite. If some oxidation has occurred during digestion the resulting arsenate compounds are formed but they are also soluble. Slowly acidify the filtrate with  $\text{HCl}$ .<sup>8</sup> Write the two equations. Is all of the arsenic in the form of  $\text{As}_2\text{S}_5$ ? Add 1 cc. 6*n*  $\text{HCl}$  in excess and pass  $\text{H}_2\text{S}$  through the solution. Do not add  $\text{H}_2\text{S}$  for too long a period as free sulfur is also precipitated. Does the  $\text{H}_2\text{S}$  increase the amount of  $\text{As}_2\text{S}_3$  precipitate? Explain.

**2. Magnesium Ammonium Arsenite,  $\text{MgNH}_4\text{AsO}_3$ .**—This colorless crystalline salt is quite soluble and a solution containing it is made by adding "magnesia mixture." (An alkaline mixture of  $\text{MgCl}_2$ ,  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$ ) to a solution of an arsenite. Can this reaction be used as a test for arsenites? Compare later with a similar test made with arsenate-ion.

**3. Reaction with Ammonium Molybdate Reagent.**—Add, to a test solution of an arsenite, sufficient 6*n*  $\text{HNO}_3$  to make acid if not already so. Now add an equal volume of ammonium molybdate reagent, and warm slightly. Is there a precipitate formed? Later compare this test with a similar one where the arsenate radical is involved.

**4.** Other reactions involving the arsenite radical will be considered in Part III in connection with non-metallic radicals.

**5.** Discuss the possibility of precipitating metallic arsenic from its solutions by other metals.

<sup>8</sup> Test with litmus; do not guess. Because a slight precipitate may have formed it does not necessarily indicate that the solution is acid. All of the precipitate is desired, and not a part.

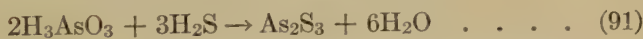
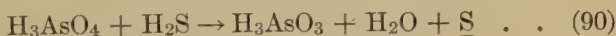
## EXERCISES

1. Write an equation for the oxidation of  $(\text{NH}_4)_3\text{AsO}_3$  into  $(\text{NH}_4)_3\text{AsO}_4$  by a polysulfide and show the oxidation-reduction process by the electron-transfer method.
2. In order to understand more clearly the radicals that are present in the mono- and polysulfides, look up the preparation of colorless-ammonium sulfide,  $(\text{NH}_4)_2\text{S}$ , and the yellow polysulfide,  $(\text{NH}_4)_2\text{S}_x$ . Can the ordinary sulfide act as an oxidizing agent?
3. Show by equilibrium constants how the sulfides of arsenic can be precipitated by  $\text{H}_2\text{S}$  from a suspension of  $\text{As}_2\text{O}_3$ . What does the numerical value of  $K_{\text{sp}}$  for  $\text{As}_2\text{S}_3$  indicate concerning the degree of its solubility?
4. In obtaining a precipitate from a solution of the sulfarsenite or sulfarsenate, how might you determine whether the solid contains the sulfides of arsenic or merely free S?

ARSENIC-ION,  $\text{As}^{+5}$  (COLORLESS)

Since an aqueous solution of  $\text{As}_2\text{O}_5$  will furnish only a small concentration of  $\text{As}^{+5}$  ions, what is going to be our best method of obtaining pentavalent arsenic?

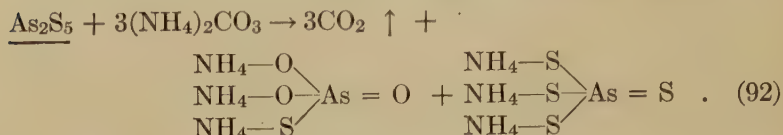
**1. Arsenic Sulfide,  $\text{As}_2\text{S}_5$ .**—Take 5 cc. test solution of an arsenate, add 5 cc. 3*n* HCl, dilute with 100 cc. water and pass  $\text{H}_2\text{S}$  through. A slow formation of  $\text{As}_2\text{S}_3$  will result, with a simultaneous precipitation of S. The equations are:



Determine if heating the solution will increase the rate of precipitation.

Again start with the same amount of test solution and water but add 10 cc. 12*n* HCl and precipitate with  $\text{H}_2\text{S}$ . Is there any change in the rate or type of precipitation where the acidity has been increased? The precipitate is mostly  $\text{As}_2\text{S}_5$  under these conditions. Refer to Plate II, *E*, for color comparison. Where the acidity with HCl is high and the solution is hot, a mixed precipitate of  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{S}_5$  results. Remember that more efficient precipitation from a solution of an arsenate results from high acidity and a hot solution. What effect will these conditions have upon the precipitation of other members of the group? Refer to the procedure for the analysis of Group II and see how this difficulty is handled.

Some of the solubilities of  $\text{As}_2\text{S}_5$  have already been considered either directly or indirectly. Summarize the facts. Especially determine the solubility in  $12n$   $\text{HCl}$ ,  $(\text{NH}_4)_2\text{S}$ ,  $(\text{NH}_4)_2\text{S}_x$  and  $(\text{NH}_4)_2\text{CO}_3$ . Write the equations. The solubility of  $\text{As}_2\text{S}_5$  in  $(\text{NH}_4)_2\text{CO}_3$  differs slightly from that of  $\text{As}_2\text{S}_3$  and is shown by:



Write the equations for the reprecipitation when the solution is made acid with  $\text{HCl}$ .

**2. Magnesium Ammonium Arsenate,  $\text{MgNH}_4\text{AsO}_4$ .**—Add alkaline magnesia mixture to a solution of sodium arsenate. The precipitate forms best in cold concentrated solutions and is  $\text{MgNH}_4\text{AsO}_4$ . When the solution is dilute, the precipitate will result very slowly and the glass frequently must be scratched in order to promote the formation of the crystals. How does this reaction differ from a similar one where the arsenite ion was involved?

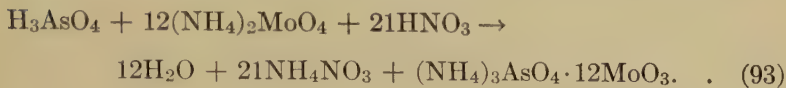
Divide the solution containing the precipitate into three parts and test the effect of (a) largely diluting with water, (b) warming without dilution, (c) adding an acid in excess.

**3. Ammonium Arsenomolybdate,<sup>9</sup>  $(\text{NH}_4)_3\text{AsO}_4 \cdot 12 \text{MoO}_3$ .**—Add sufficient  $6n$   $\text{HNO}_3$  to 5 cc. of a solution of an arsenate to make acid, and then 2 cc. in excess. Now add the ammonium molybdate reagent in small amounts until a yellow precipitate appears but not to exceed an amount equal to that of the test solution. The precipitate may slowly develop as a turbidity and resembles *D* or *E* of

<sup>9</sup> The precipitate  $(\text{NH}_4)_3\text{AsO}_4 \cdot 12 \text{MoO}_3$  is commonly referred to as ammonium arsenomolybdate. If this name is interpreted by comparison with the names of other compounds it is decidedly misleading. For example,  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is potassium ferro(us) cyanide. The iron in this compound is in the *ous* condition. In the "arsenomolybdate," however, the arsenic is in the higher valence and the compound is *ic* and not *ous*. In fact, the preliminary tests have stressed the non-formation of a precipitate with arsenite-ion and the formation with arsenate-ion. A better name for the compound might be ammonium arsenate molybdate. While it is true that the exact composition of the precipitate formed by the reaction of a soluble arsenate with the ammonium molybdate reagent is not settled, that does not justify the giving of an erroneous nomenclature to a tentative formula.



Plate I. The solution may be warmed but not boiled to assist in the formation of the precipitate. Why not boil? Is there a similar precipitate formed with arsenite-ion? The reaction is:



Take some of the molybdate reagent and make alkaline with  $6n$  NaOH. Describe the results. This test shows in part why the test cannot be made in a solution unless it is acid.<sup>10</sup> Test the solubility of some of the ammonium arsenomolybdate precipitate in  $\text{NH}_4\text{OH}$  and NaOH.

4. Other tests for arsenates will be given in connection with arsenic acid in the section on anions.

### EXERCISES

1. Have you any data that will enable you to determine the relative solubilities of  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{S}_5$  in water. Compare their solubilities in  $6n$  HCl. How do you account for the fact that  $\text{H}_2\text{S}$  does not precipitate  $\text{As}_2\text{S}_5$  from a cold slightly acid solution of an arsenate?

2. Where  $\text{As}_2\text{S}_3$  or  $\text{As}_2\text{S}_5$  is precipitated from solutions of arsenates or arsenites by  $\text{H}_2\text{S}$ , what electron transfers are involved? Is a precipitate with  $\text{H}_2\text{S}$  obtained the more readily from an arsenate or an arsenite? Why? Will an oxidizing or reducing agent accelerate the precipitation?

3. What would be the effect of first passing  $\text{SO}_2$  through a solution of an arsenate before using  $\text{H}_2\text{S}$ ? Write the equation.

4. Why is a large excess of reagent used in the test with ammonium molybdate? Answer from as many points of view as possible.

### ANTIMONOUS-ION, $\text{Sb}^{+3}$ (COLORLESS)

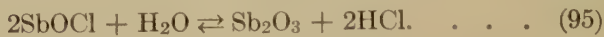
Antimony forms four series of salts, quite analogous to those of arsenic. The valences are  $+3$  and  $+5$  and both hydroxides are amphoteric.  $\text{Sb}(\text{OH})_3$ , unlike  $\text{As}(\text{OH})_3$ , is slightly basic, while  $\text{Sb}(\text{OH})_5$  is acidic. Suggest a possible source of  $\text{Sb}^{+3}$ . Which hydroxide should dissolve the more readily in bases? Should  $\text{AsCl}_3$  or  $\text{SbCl}_3$  be the more easily hydrolyzed?  $\text{SbCl}_3$  or  $\text{SbCl}_5$ ?

A solution of  $\text{SbCl}_3$  can be made by dissolving  $\text{SbCl}_3$  in  $6n$  HCl. Recall how a solution of  $\text{AsCl}_3$  was made by slowly digesting with

<sup>10</sup> It is assumed that  $\text{HNO}_3$  is in large excess. Where there is much HCl present a special method of making the molybdate is required.



12*n* HCl. Take 5 cc. of a test solution of SbCl<sub>3</sub> and dilute with water until a white turbidity results. The reactions are:



The white precipitate SbOCl is antimony oxychloride, sometimes referred to as antimony subchloride. What can be inferred from the above about the solubility of Sb<sub>2</sub>O<sub>3</sub> in HCl?

**1. Antimonous Sulfide, Sb<sub>2</sub>S<sub>3</sub>.**—Take 5 cc. test solution of SbCl<sub>3</sub>, add 5 cc. 6*n* HCl, dilute with 100 cc. water and precipitate with H<sub>2</sub>S<sup>11</sup>.

Describe the precipitate and compare with *J* of Plate II. This color is usually referred to as orange-red. Filter and wash with hot water. Has the precipitate any tendency to form a colloidal suspension? Test the solubility of antimony trisulfide Sb<sub>2</sub>S<sub>3</sub> in 6*n* HCl. Also test the solubility of portions of the precipitate in NaOH, NH<sub>4</sub>OH, (NH<sub>4</sub>)<sub>2</sub>S, and (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> or Na<sub>2</sub>S<sub>x</sub>. The solubility in all monosulfides should be inappreciable, but it should be very complete in the polysulfide. The oxidation by the polysulfide is shown by:



Filter to remove the S and reprecipitate from the filtrate by adding 6*n* HCl dropwise. Warm as precipitation progresses. Write the equation and show what precipitates may be present. The solution of the sulfantimonate will decompose upon standing as with the corresponding arsenic compound. Filter off the Sb<sub>2</sub>S<sub>5</sub> and keep it for a later comparison with the precipitate obtained from SbCl<sub>5</sub>.

Test the solubility of Sb<sub>2</sub>S<sub>3</sub> or Sb<sub>2</sub>S<sub>5</sub> in (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> to determine whether a separation from As<sub>2</sub>S<sub>3</sub> and As<sub>2</sub>S<sub>5</sub> can be made by this method.

**2. Precipitation of Sb° from Solutions by Metals.**—Antimony is readily deposited from solutions by more electropositive metals. If a piece of iron is placed in a solution containing antimony and tin chlorides, which will be deposited the more readily? Test

<sup>11</sup> If by this dilution there is slight hydrolysis do not remove the precipitate. The H<sub>2</sub>S will take care of it for you. Explain.

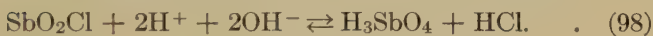
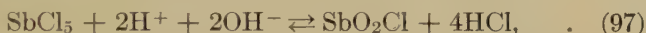
various concentrations to see if you can deposit the antimony and only a trace of the tin. Another characteristic difference between the deposition of Sb and Sn is shown by the following: Take a solution containing antimony and tin chlorides and add an excess of a few drops of HCl. Place in an evaporating dish in the bottom of which is a small square of platinum foil. Place a piece of pure Zn<sup>12</sup> on the foil. Notice the stain of antimony on the foil and the black particles of metallic tin on the zinc<sup>13</sup> and in the solution.

## EXERCISES

1. State one method that we have developed whereby Sb<sup>+3</sup> can be separated from (a) Pb<sup>++</sup>, (b) As<sup>+3</sup>, (c) Hg<sup>++</sup>.
2. Explain how H<sub>2</sub>S can precipitate Sb<sub>2</sub>S<sub>3</sub> from a suspension of SbOCl.
3. What will be the effect of increasing the acidity upon the reaction proposed in "2"?
4. Compare the solubilities of Sb<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>3</sub> in 6*n* or 12*n* HCl.
5. How can the hydrolysis of a solution of SbCl<sub>3</sub> be prevented or retarded?
6. Will a higher or a lower acid concentration be required to retard the hydrolysis of SbCl<sub>3</sub> to the same extent as in an equimolar solution of AsCl<sub>3</sub>?

ANTIMONIC-ION, Sb<sup>+5</sup> (COLORLESS)

The hydrolysis of SbCl<sub>5</sub> is shown by the following:

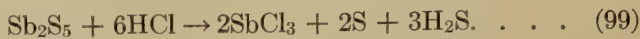


**1. Antimonic Sulfide, Sb<sub>2</sub>S<sub>5</sub>.**—Precipitate Sb<sub>2</sub>S<sub>5</sub> by H<sub>2</sub>S from a test solution of SbCl<sub>5</sub> which contains an excess of HCl. Take a solution of SbCl<sub>5</sub> which is partly hydrolyzed and precipitate with H<sub>2</sub>S. Filter either precipitate and wash with hot water. Compare the color with *J* of Plate II, and also recall the precipitate of Sb<sub>2</sub>S<sub>5</sub> previously obtained by precipitating the sulfantimonate solution in connection with the antimonous-ion. Test the solubility of Sb<sub>2</sub>S<sub>5</sub> in 12*n* HCl, (NH<sub>4</sub>)<sub>2</sub>S, (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. Be sure to determine that Sb<sub>2</sub>S<sub>5</sub> is soluble in (NH<sub>4</sub>)<sub>2</sub>S as well as

<sup>12</sup> Commercial zinc contains too much carbon and other impurities.

<sup>13</sup> The [H<sup>+</sup>] of the solution determines where the Sn is deposited; if it is small the deposit of Sn will be mostly on the Zn, and if it is high the deposit will be on the Pt.

$(\text{NH}_4)_2\text{S}_x$ . When  $\text{Sb}_2\text{S}_5$  dissolves in  $12n$   $\text{HCl}$  it is reduced to  $\text{Sb}_2\text{S}_3$ , as shown by the equation:



What was the main purpose of the polysulfide when used in conjunction with  $\text{Sb}_2\text{S}_3$ ? Test the solubility in  $(\text{NH}_4)_2\text{CO}_3$ . In the solubility tests, wherever a solution has resulted by the addition of an alkali solvent, filter and reprecipitate by making acid with  $\text{HCl}$ .

### EXERCISES

1. Is antimonious acid a strong acid? Upon what do you base your answer? How does it compare with antimonous acid?
2. Compare the solubilities of  $\text{Sb}_2\text{S}_3$  with those of  $\text{Sb}_2\text{S}_5$  in (a)  $6n$   $\text{HNO}_3$ , (b)  $(\text{NH}_4)_2\text{S}_x$ , (c)  $(\text{NH}_4)_2\text{S}$ , (d)  $(\text{NH}_4)_2\text{CO}_3$ .
3. Will metallic antimony be precipitated by other metals more readily from an acid solution of  $\text{SbCl}_5$  or  $\text{SbCl}_3$ ?

### STANNOUS-ION, $\text{Sn}^{++}$ (COLORLESS)

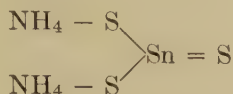
Tin forms two hydroxides,  $\text{Sn}(\text{OH})_2$  and  $\text{Sn}(\text{OH})_4$  and, since both are amphoteric, there are four series of compounds as with arsenic and antimony. Stannous hydroxide is chiefly a weak base, while stannic hydroxide reacts for the most part as an acid. The solubilities in acids and bases should therefore be very similar to those of antimony. From the location of  $\text{Sb}$  and  $\text{Sn}$  in the periodic classification, decide whether their positions are in harmony with the amphoteric characteristics of the two elements.

One general characteristic of stannous compounds is that they readily change to stannic. Are all "ous" compounds equally unstable? What type of reactions can in general be accomplished by adding stannous compounds? When tin dissolves in  $\text{HCl}$ , which chloride will be formed? Write the equation.

**1. Stannous Sulfide,  $\text{SnS}$ .**—Take 5 cc. test solution of  $\text{SnCl}_2$ ,<sup>14</sup> add 5 cc.  $6n$   $\text{HCl}$ , dilute with 100 cc. water and precipitate with  $\text{H}_2\text{S}$ . Filter and wash with hot water. The precipitate,  $\text{SnS}$ , is brown but may be lighter in color because of the presence of  $\text{SnS}_2$ , which is yellow. Compare with Plate II, *G* and *H*. How do you account for the presence of  $\text{SnS}_2$ ? Test the solubility of the

<sup>14</sup> Stannous chloride solution must be acid and also contain metallic tin. Why? The white deposit consists of oxidation products.

precipitate in  $12n$  HCl,  $(\text{NH}_4)_2\text{S}$  and one of the polysulfides. It should be practically insoluble in the monosulfide. The structural formula for ammonium sulfostannate is:



Write the equation to show how the sulfostannate is formed. Filter the solution and reprecipitate by making acid with HCl. Write the equation. Will  $\text{SnS}$  be present in this precipitate? What else is present? Reserve this precipitate until we have finished with stannous-ion.

Test the solubility of  $\text{SnS}$  in  $(\text{NH}_4)_2\text{CO}_3$ . It should be insoluble.

**2. Stannous Chloride,  $\text{SnCl}_2$ .**—This chloride readily changes to  $\text{SnCl}_4$  and can, therefore, be used to reduce certain compounds. Take a solution of  $\text{HgCl}_2$  and add, dropwise, a solution of  $\text{SnCl}_2$  which you are positive is in the lower state of valence. White  $\text{HgCl}$  and bluish-black  $\text{Hg}$  should result in steps. What radicals can be determined by means of this test? Write the equations. The test is more satisfactory when the two precipitates are obtained instead of either the  $\text{HgCl}$  or the  $\text{Hg}$ . There are other combinations that will give a white precipitate but will not darken later.

**3. Metallic Tin** is readily precipitated from  $\text{SnCl}_2$  solutions by the proper metals. Suggest three.

### EXERCISES

1. Locate arsenic, antimony and tin in the periodic classification of the elements. Which valence has been used in the three cases? Is this rule followed in placing all of the elements?

2.  $\text{Sn}(\text{OH})_2$  is insoluble in an excess of  $\text{NH}_4\text{OH}$ , but readily dissolves in  $\text{NaOH}$ . What does this show?

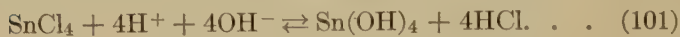
3. Write an expression for the ionization constant for  $\text{H}_2\text{SnO}_2$  where it ionizes as a dibasic acid.

4. Show why a solution of sodium stannite will be at least slightly alkaline.

5. When a solution of sodium stannite is slowly neutralized with HCl, will a precipitate form before the solution is neutral? Will there be a precipitate when the solution is strongly acid?

STANNIC-ION,  $\text{Sn}^{+4}$  (COLORLESS)

Test a solution of  $\text{SnCl}_4$  for hydrolysis by dissolving in water and boiling if necessary. Should  $\text{SnCl}_2$  or  $\text{SnCl}_4$  hydrolyze the more readily? The reactions are:



**1. Stannic Sulfide,  $\text{SnS}_2$ .**—Precipitate  $\text{SnS}_2$  from 5 cc. test solution of  $\text{SnCl}_4$  acidified with 5 cc. 6*n* HCl and diluted with 100 cc. water. Compare the color with that of  $\text{SnS}$  obtained in the section on stannous-ion. Test the solubility in 12*n* HCl. There is no reduction by the concentrated HCl as in the case of  $\text{Sb}_2\text{S}_5$ . The solvent action of the polysulfides has already been discussed.  $\text{SnS}_2$  is soluble also in the monosulfide. Compare with  $\text{SnS}$ . Test the solubility in  $(\text{NH}_4)_2\text{CO}_3$ . Filter and make acid with HCl. Explain the result.

**2. Precipitation of Metallic Tin** by metals that are more electro-positive is possible from a solution of  $\text{SnCl}_4$  where there is sufficient HCl present. The reduction can go to  $\text{SnCl}_2$  or to metallic  $\text{Sn}^0$ .

## EXERCISES

1. Can  $\text{SnCl}_4$  be used in the test with  $\text{HgCl}_2$  to identify mercuric-ion? Explain.
2. Compare the solubilities of the sulfides of antimony and tin in all of the reagents that were used in the preliminary tests.
3. What are some of the methods that can be used to separate antimony from tin? Arsenic from tin? Arsenic from antimony?

## SUMMARY OF REACTIONS OF THE IONS IN GROUP II THAT ARE OF IMPORTANCE IN ANALYTICAL PROCEDURE

In precipitating the members of Group II as sulfides the importance of the proper acidity has been stressed. With the exception of arsenates, the desirable acidity has been approximately 0.3*n* with hydrochloric acid. In this concentration the most soluble sulfides of the group, namely, those of lead and tin, should



be efficiently precipitated. But the question naturally arises: Why should the solution be acid if it increases the solubility of all of the sulfides? Even though the loss may be insignificant it should be avoided if possible.

There are many points involved in this issue, but the most important one is undoubtedly the effect of acidity on the solubility of compounds of members of succeeding groups which may be present when Group II is precipitated. Beginners may consider that only the sulfides of this group are formed during the precipitation with hydrogen sulfide. The fact is, however, that there are concentrations of the sulfides of all of the metallic radicals present but that the members of Group II are the only ones precipitated in a solution containing  $0.3n$  HCl. Analyzing a step further, this means that the solubility products of the members of Group II have been the only ones exceeded. Again, since the available  $[S^-]$  is the same for all positive radicals present, the solubility product of the most soluble sulfide of Group II must be less than that for any member of the succeeding groups.

The values of the solubility products of the sulfides increase in the following order:  $As_2S_3$ ,  $HgS$ ,  $CuS$ ,  $Sb_2S_3$ ,  $Bi_2S_3$ ,  $SnS_2$ ,  $CdS$ ,  $PbS$ ,  $SnS$ ,  $(ZnS, CoS, NiS)$ ,  $FeS$ ,  $MnS$ .<sup>15</sup>

It is evident that with a common concentration of  $S^-$  a precipitate will be formed when  $K_{SP}$  is exceeded, and this in turn will depend both upon the magnitude of the values of  $K_{SP}$  and the concentrations of metallic radicals present. If, in practice solutions, the concentration of metallic radicals does not differ greatly in normality, the order of precipitation will be the same as the order of values of  $K_{SP}$ . The following table gives several of these values.

<sup>15</sup> It is interesting to note that the order of metals in the electromotive series is almost a duplicate of the order of sulfide solubilities, the most electropositive being the most soluble. The sulfides have been given in the order commonly found in reference books. However, the most recent solubility product measurements place  $CoS$ ,  $NiS$  and  $ZnS$  with increasing values and in the order given. If  $ZnS$  is the first to precipitate in Group II with insufficient acid, it is due to other causes than solubility-product relationships. We have observed  $NiS$  precipitate in Group II but never the traditional  $ZnS$ .

TABLE XV

SOLUBILITY-PRODUCT CONSTANTS FOR SEVERAL SULFIDES AT APPROXIMATELY  
18°

Sulfide	Solubility-product
HgS	$4 \times 10^{-54}$
CuS	$2 \times 10^{-47}$
CdS	$3.6 \times 10^{-29}$
PbS	$5 \times 10^{-29}$
CoS	$3 \times 10^{-26}$
NiS	$1.4 \times 10^{-24}$
ZnS	$1.2 \times 10^{-23}$
FeS	$3.7 \times 10^{-19}$

The following table shows the maximum acidity that may be present for a satisfactory precipitation of the sulfides of the members of Group II and some of Group III.

TABLE XVI

THE MAXIMUM ACIDITY IN WHICH CERTAIN SULFIDES WILL BE SATISFACTORILY PRECIPITATED

Sulfide	Maximum Acidity
As <sub>2</sub> S <sub>3</sub> .....	12 <i>n</i> HCl
Hg S } .....	7.5 HCl
Cu S } .....	3.7 HCl
Sb <sub>2</sub> S <sub>3</sub> .....	3.7 HCl
Bi <sub>2</sub> S <sub>3</sub> } .....	2.5 HCl
SnS <sub>2</sub> } .....	0.7 HCl
CdS.....	0.7 HCl
PbS } .....	0.31 HCl
SnS } .....	0.02 HCl
ZnS.....	0.02 HCl
CoS } .....	0.001 HCl
NiS } .....	0.0001 HCl
FeS } .....	
MnS } .....	

The separation of Groups II and III is made between SnS and ZnS. It can be seen that by allowing an acid concentration of 0.3*n* HCl we are working with about the maximum acidity that can be present without an excessive amount of PbS and SnS dissolving. What would be the result of decreasing the acidity to nearly 0.02*n*? Why is not the division made between PbS and CdS where there is a greater change in normality? ( $0.7 - 0.31 = 0.39$  compared with  $0.31 - 0.02 = 0.29$ .)

Considering the same question from another standpoint, we can involve the solubility products of the sulfides and the ionization constant of  $\text{H}_2\text{S}$ . If we are to prevent the precipitation of  $\text{ZnS}$  and the more soluble sulfides we must keep  $K_{\text{SP}} = [\text{Zn}^{++}] [\text{S}^-]$  from being exceeded. Now the  $[\text{Zn}^{++}]$  is fixed by the amount of radical in the sample, so that the control lies in the variation of  $[\text{S}^-]$  from the  $\text{H}_2\text{S}$ . By considering the dissociation constant of  $\text{H}_2\text{S}$ ,

$$\frac{[\text{H}^+]^2 [\text{S}^-]}{[\text{H}_2\text{S}]} = K_{\text{ion}},$$

it can be seen that as  $[\text{H}^+]$  increases  $[\text{S}^-]$  must decrease. Therefore, to prevent  $\text{ZnS}$  from precipitating,  $[\text{H}^+]$  must be made large enough to decrease  $[\text{S}^-]$  to a point where  $[\text{Zn}^{++}] [\text{S}^-] = K_{\text{SP}}$  will not be exceeded. This, we have stated, can be successfully done by making the acid concentration greater than  $0.02n$  or, in actual practice,  $0.3n$ .

Having decided upon  $0.3n$   $\text{HCl}$  as the desirable acid concentration to separate the two groups, we encounter a difficulty in the failure to precipitate, in this weakly acid solution, the sulfides of arsenic from a solution of arsenates. The preliminary work showed that in cold  $0.3n$  acid solution of an arsenate no precipitation occurred with  $\text{H}_2\text{S}$  until after a long period of time, while in a cold concentrated acid solution we obtained a small amount of  $\text{As}_2\text{S}_5$ . When, however, the strongly acid solution was heated, a mixture of  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{S}_5$  resulted. This high acidity, however, will certainly prevent the precipitation of most of the other members of Group II.

Both reduction of arsenates and precipitation of the group must be accomplished, hence in our procedure the arsenate is reduced first by means of  $\text{H}_2\text{S}$  in a hot concentrated solution; then this is diluted with water with the consequent precipitation of most of the remaining sulfides of the group. After the solution has been cooled,  $\text{H}_2\text{S}$  is again passed through, and by filtering off the precipitate and running  $\text{H}_2\text{S}$  through the clear filtrate we can make certain that precipitation has been complete. The details of the procedure are often varied but it is essentially a precipitation in (a) a hot concentrated solution, (b) a hot dilute solution, and (c) a cold dilute solution.

After Group II is precipitated it can be subdivided into two

groups by the action of sodium or ammonium polysulfides upon the precipitated sulfides. The preliminary tests developed the fact that when the monosulfide is used the sulfides of  $\text{As}^{+3}$ ,  $\text{As}^{+5}$ ,  $\text{Sb}^{+5}$  and  $\text{Sn}^{+4}$  will be dissolved while by using a polysulfide the sulfides of  $\text{Sb}^{+3}$  and  $\text{Sn}^{+2}$  will be oxidized and will go into solution as well. Subdivision *A* will then contain the sulfides of mercury(ie), lead, bismuth, copper and cadmium, while subdivision *B* will contain the soluble sulfosalts of arsenic, antimony and tin.

It was found that the sulfosalts are very unstable and for that reason it is better to proceed first with the analysis of subdivision *B*. This subdivision, also known as the tin group, is strongly alkaline and the sulfides of arsenic, antimony and tin will be reprecipitated when the solution is made acid. Care must be exercised in adding the acid because the solubility tests showed that the sulfides are soluble in  $6n$   $\text{HCl}$  or even in a more dilute acid if sufficient time is given.

Since the sulfides of arsenic dissolve in strong ammonium carbonate while those of antimony and tin do not, a method is available for the separation of arsenic from antimony and tin. The reprecipitation and identification of arsenic sulfide can be made by adding  $\text{HCl}$  in excess.

Antimony and tin sulfides are soluble in  $\text{HCl}$ , but by carefully controlling the acidity it is possible first to put both sulfides in solution and then fractionally reprecipitate them.

In the analysis of subdivision *A*, the copper group, the first separation makes use of the small solubility of  $\text{HgS}$  in  $6n$   $\text{HNO}_3$ . By digesting the sulfides of  $\text{Hg}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Bi}^{+3}$ ,  $\text{Cu}^{++}$  and  $\text{Cd}^{++}$  with  $6n$   $\text{HNO}_3$ , the residue will consist of  $\text{HgS}$  and  $\text{S}$ . Mercury can then be identified by dissolving the sulfide in aqua regia and making a test with  $\text{SnCl}_2$  solution. The solution containing the soluble nitrates of lead, bismuth, copper and cadmium can be further subdivided by removing lead as a sulfate. The solution of  $\text{PbSO}_4$  can then be accomplished by digesting with  $\text{NH}_4\text{Ac}$  and  $\text{HAc}$ , and lead finally identified as  $\text{PbCrO}_4$ .

Bismuth can be separated from the remaining solution by adding  $\text{NH}_4\text{OH}$  in excess because copper and cadmium form soluble ammonia complexes while bismuth will be precipitated as  $\text{Bi}(\text{OH})_3$ . Bismuth hydroxide is readily soluble in  $\text{HCl}$  and the chloride can be tested by adding water or a solution of sodium stannite.

The blue color of the copper complex is very characteristic and



can be used as a preliminary test for copper. The characteristic reddish-brown of  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$  is more definite, however. The white precipitate of  $\text{Cd}_2[\text{Fe}(\text{CN})_6]$  will identify cadmium unless copper is present. To make a test for cadmium in the presence of copper an interesting application of the difference in certain instability constants is made use of. If  $\text{H}_2\text{S}$  were passed through the blue solution containing  $\text{Cu}(\text{NH}_3)_4^{++}$  and  $\text{Cd}(\text{NH}_3)_4^{++}$ , a black precipitate of  $\text{CuS}$  would obscure that of the yellow  $\text{CdS}$ . If, however, a solution of  $\text{KCN}$  is first added until the solution of ammonia complexes is decolorized, another pair of complex radicals is formed  $[\text{Cu}(\text{CN})_4]^{-3}$  and  $[\text{Cd}(\text{CN})_4]^{-2}$ , in which the ionization of the first is extremely small and that of the second is great enough, so that the resulting  $[\text{Cd}^{++}]$ , together with the  $[\text{S}^-]$  when  $\text{H}_2\text{S}$  is passed through the solution, will exceed the solubility product for  $\text{CdS}$ . The yellow precipitate of  $\text{CdS}$  can therefore be obtained even in the presence of the copper cyanide complex.

#### PROCEDURE FOR THE ANALYSIS OF A PRACTICE SOLUTION CONTAINING GROUP II

**Precipitation of Group II.**—The practice solution will contain the radicals of Group II in a clear solution.<sup>a</sup> Make a preliminary side test for  $\text{Hg}^{++}$  by means of the  $\text{SnCl}_2$  reagent. Dilute in a flask the portion<sup>b</sup> of the solution to be analyzed with water to 100 cc. Test for degree of acidity<sup>c</sup> and make the proper correction by adding either water or 6*N*  $\text{HCl}$ . Heat nearly to boiling and precipitate for ten minutes with  $\text{H}_2\text{S}$ .<sup>a</sup> Disconnect the flask from the gas line and, without removing the stopper, cool under the tap with water. Filter, reheat the filtrate and reprecipitate as before for another ten-minute period. Cool, and if there is no precipitate<sup>e</sup> in the flask, either discard the filtrate if Group II is the only group present, or combine it with the washings of the group precipitate and reserve for Group III.<sup>f</sup> If during the second heating and treatment with  $\text{H}_2\text{S}$ , a further precipitate is formed, the process is to be repeated until a filtrate is obtained that does not give a precipitate with  $\text{H}_2\text{S}$ .<sup>g</sup> The group precipitate, which may contain precipitates of  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{CdS}$ ,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_5$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_5$ ,  $\text{SnS}$ ,  $\text{SnS}_2$  and  $\text{S}$ , is washed with a little hot water containing some  $\text{H}_2\text{S}$  and a few drops of  $\text{NH}_4\text{NO}_3$  solution.

**Separation of Subdivisions A and B.**—Remove the mixed sulfides to an evaporating dish,<sup>h</sup> add 5–10 cc.<sup>i</sup>  $\text{Na}_2\text{S}_x$  solution, digest



for at least ten minutes<sup>j</sup> and stir with a glass rod to promote solution. Do not warm the solution unless you are certain that mercury is absent.<sup>k</sup> Dilute<sup>l</sup> with water, filter and proceed with the analysis of subdivision *B* which is in the filtrate<sup>m</sup> and consists of solutions of  $\text{Na}_3\text{AsS}_4$ ,  $\text{Na}_3\text{SbS}_4$  and  $\text{Na}_2\text{SnS}_3$ .

**Reprecipitation and Analysis of Subdivision *B*.**—Carefully reprecipitate the sulfides of subdivision *B* by adding  $6n$   $\text{HCl}$  in small portions until the solution is just acid. Heat slightly between additions of acid and stir thoroughly. Filter and wash once with hot water and discard filtrate and washings. The precipitate contains  $\text{As}_2\text{S}_5$ ,  $\text{Sb}_2\text{S}_5$ ,  $\text{SnS}_2$  and  $\text{S}$ .<sup>n</sup>

**Separation and Identification of Arsenic.**—Transfer the precipitate to an evaporating dish and digest for ten to fifteen minutes with concentrated  $(\text{NH}_4)_2\text{CO}_3$  solution containing a small amount of the solid reagent. Stir frequently during the process. Dilute with 3 cc. water, filter and wash once with water. The residue contains  $\text{Sb}_2\text{S}_5$ ,  $\text{SnS}_2$  and  $\text{S}$ . Arsenic is in solution in the filtrate in two soluble salts  $(\text{NH}_4)_3\text{AsO}_3\text{S}$  and  $(\text{NH}_4)_3\text{AsS}_4$ . Reprecipitate arsenic pentasulfide from the solution by adding  $6n$   $\text{HCl}$  until acid, and pass  $\text{H}_2\text{S}$  through to obtain a maximum amount of  $\text{As}_2\text{S}_5$ , the test for arsenic.

**Identification of Antimony and Tin.**—Leach<sup>o</sup> the residue which is still on the filter paper with 12 cc.  $12n$   $\text{HCl}$  or transfer the residue to an evaporating dish and digest with the same amount of acid. The solids can be stirred and warmed slightly<sup>p</sup>. Do not boil because we must retain, as far as possible, the 12 cc.  $12n$   $\text{HCl}$ . Filter and wash once with water. The residue consists of  $\text{S}$  and possibly some  $\text{As}_2\text{S}_5$  which was not dissolved in  $(\text{NH}_4)_2\text{CO}_3$  owing to imperfect solution. Reserve this residue so that it can be used in retesting for arsenic if only a trace was obtained. Dilute the filtrate with water to 65 cc.<sup>q</sup>, place in a 200-cc. flask, heat to boiling and place in a beaker of boiling water. Now pass  $\text{H}_2\text{S}$  through the solution. The orange-red precipitate of  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_5$  should soon appear. This constitutes the test for antimony. Continue precipitation until it appears to be complete. Allow the hot solution to cool and the yellow  $\text{SnS}_2$ , the test for tin, will be formed above the antimony precipitate which by this time has settled. The two precipitates are so distinctive in color that there should be no difficulty in detecting the one in the presence of the other. Where the antimony is present in small amounts it is sometimes better to

filter the red sulfides from the hot solution, thereby coloring the filter paper a distinct red. When the solution has cooled, filter through another paper and, even though the tin may be in a small amount, a yellow color should appear on the paper.<sup>r</sup> Additional confirmatory tests for antimony and tin are given in the optional tests. This fundamental separation will be conclusive in the majority of analyses.

**Analysis of Subdivision A, Identification of Mercury.**—The precipitate consists of  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{CdS}$  and  $\text{S}$ . First transfer this precipitate to an evaporating dish, add 10 cc. 6*N*  $\text{HNO}_3$  and digest for ten to fifteen minutes. If mercury is not present the solution may be warmed.<sup>s</sup> Filter and wash once with hot water. The residue consists of  $\text{HgS}$  and  $\text{S}$  and in the filtrate are the soluble nitrates,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Bi}(\text{NO}_3)_3$ ,  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Cd}(\text{NO}_3)_2$ . Digest the residue of  $\text{HgS}$  and  $\text{S}$  in aqua regia to which a few crystals of  $\text{KClO}_3$  have been added if necessary. Concentrate by boiling to about 1 cc. to remove the excess  $\text{Cl}_2$ , dilute with 5 cc. water and filter to remove sulfur. Now add, dropwise,  $\text{SnCl}_2$  solution. White  $\text{HgCl}$  which gradually darkens as  $\text{Hg}$  is liberated, confirms mercury.

**Identification of Lead.**—Returning to the filtrate containing the soluble nitrates,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Bi}(\text{NO}_3)_3$ ,  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Cd}(\text{NO}_3)_2$ ; place in an evaporating dish and add a volume of concentrated  $\text{H}_2\text{SO}_4$  equal to one-third the volume of the nitrate solution present.<sup>t</sup> Evaporate under a hood until  $\text{SO}_3$  fumes appear or until the volume of the solution has been reduced to about 5 cc.<sup>u</sup>, cool, pour into another evaporating dish containing 10 cc.<sup>v</sup> water, allow the  $\text{PbSO}_4$  to settle and decant the liquid through a filter. Wash once with water and pour washings through the same paper.<sup>w</sup> Digest the  $\text{PbSO}_4$  with a concentrated solution of  $\text{NH}_4\text{Ac}$  to which a few drops of concentrated acetic acid have been added. Stir and warm very gently and add more acetic acid as the volume of liquid is reduced. One-half hour may be required before sufficient solution has been accomplished. Decant some of the liquid into a test tube, and add an equal volume of water and a few drops of  $\text{K}_2\text{CrO}_4$  solution. The yellow precipitate of  $\text{PbCrO}_4$  is the final test for lead.

**Identification of Bismuth.**—The strongly acid solution containing the soluble sulfates of  $\text{Bi}$ ,  $\text{Cu}$  and  $\text{Cd}$  is made alkaline (use litmus) with concentrated  $\text{NH}_4\text{OH}$ . Filter off the white  $\text{Bi}(\text{OH})_3$

and, without washing, place the filter paper and its contents in another filter funnel which is perfectly dry.<sup>z</sup> Obtain a small beaker with cold water which has stood long enough to eliminate any pronounced water currents and also a test tube containing cold, freshly prepared  $\text{Na}_2\text{SnO}_2$  solution.<sup>y</sup> Now pour over the precipitate of  $\text{Bi}(\text{OH})_3$  about 12 drops of 12*n*  $\text{HCl}$  and catch 2 drops of the concentrated  $\text{BiCl}_3$  solution in the water and another 2 drops in the  $\text{Na}_2\text{SnO}_2$  solution. The first will give a white precipitate of  $\text{BiOCl}$  and the second a grayish-black precipitate of **Bi**. Both tests confirm the presence of bismuth.

**Identification of Copper.**—The alkaline filtrate from the  $\text{Bi}(\text{OH})_3$  separation will be a deep blue on account of the presence of  $\text{Cu}(\text{NH}_3)_4^{++}$  ions. This serves as a preliminary test for copper. The presence of copper can be confirmed by taking 2 cc. of the filtrate, making acid with concentrated acetic acid and adding a few drops of  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . A reddish-brown precipitate<sup>z</sup> of  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$  confirms copper. If copper is not present the white precipitate of  $\text{Cd}_2[\text{Fe}(\text{CN})_6]$  will appear and may be considered as the final test for cadmium, as it is often more satisfactory than the  $\text{CdS}$  obtained later. This is especially true if the cadmium sulfide is contaminated with  $\text{HgS}$  or  $\text{PbS}$ .

**Identification of Cadmium.**—Returning to the ammoniacal filtrate containing  $\text{Cu}(\text{NH}_3)_4^{++}$  and  $\text{Cd}(\text{NH}_3)_4^{++}$ , add, dropwise,  $\text{KCN}$  solution until decolorized and then an excess of 5 drops. Pass  $\text{H}_2\text{S}$  through the solution. The yellow precipitate  $\text{CdS}$ , confirms the presence of cadmium.<sup>1a</sup>

## NOTES ON THE PROCEDURE FOR THE ANALYSIS OF GROUP II

If a white precipitate forms when any of the solutions are diluted either before or during precipitation it is an indication of the presence of  $\text{BiOCl}$ ,  $\text{SbOCl}$  or hydrolysis products of tin, and subsequent identification for bismuth, antimony and tin should be closely followed.

By noting carefully the colors of the precipitates as they are formed, some idea of the radicals present may be gained. Care must be exercised, however, because mercury and antimony, especially the former, often give a series of precipitates which would lead one to infer that several other radicals were present.

a. If the solution contains a sediment due to hydrolysis or reduction, do not filter but precipitate with  $\text{H}_2\text{S}$  in the presence of the sediment. Where a part of the sample is analyzed at one time be certain that the sediment is equally distributed. Never use the clear supernatant liquid of a sample for

one analysis and the part with the sediment for a duplicate analysis. When  $\text{H}_2\text{S}$  is passed through the turbid liquid there will be a gradual change of the sediment containing the hydrolysis products to the more insoluble sulfides.

b. A 25-30-cc. sample is generally supplied and of such a concentration that one-half can be taken for analysis, and the other half reserved for a duplicate analysis or for other reference purposes. The preliminary test for  $\text{Hg}^{++}$  is made so that the proper procedure with  $\text{Na}_2\text{S}_x$  can be determined.

c. The solution must be  $0.3n$  with  $\text{HCl}$ , and this condition is not to be a matter of guesswork. Of course, the solution can be evaporated to dryness, diluted to 100 cc. and then 5 cc.  $6n$   $\text{HCl}$  added. Although this procedure may be necessary in the complete analysis of unknowns where objectionable acids may be present, at this period of our work this method is too slow. The best method is to test acidity with an indicator which has a gradual color change instead of a sharp one like litmus or phenolphthalein. Methyl violet is frequently used for this purpose, but the color change is very unsatisfactory and the solution is very unstable and also precipitates certain metallic ions. The best indicator is acid cresol red, and this should be used whenever obtainable. The La Motte Chemical Products Co. of Baltimore, Md., can furnish this indicator. The color changes are shown in Plate II, Q, and the acidity of the solution should be determined as outlined on page 109, which follows Plate II.

d. In precipitating with  $\text{H}_2\text{S}$  it is very inefficient to bubble the gas through at atmospheric pressure. Not only is most of the gas wasted but the precipitating action can be increased materially by increasing the pressure to that of the gas line. A good method for precipitation is to fit a one-hole rubber stopper to the flask and pass through it a glass bend which reaches nearly to the surface of the liquid. To precipitate, attach the supply-line rubber connection to the glass bend, loosen the stopper slightly to permit the air to escape and turn on the  $\text{H}_2\text{S}$ . In a minute or so the air will be displaced by the  $\text{H}_2\text{S}$  and the stopper can be pushed down. Leave the gas turned on. Notice that the glass tube is lowered nearly to touch the surface when the stopper is pushed in. If the flask is rotated occasionally without disconnecting from the supply line no other attention is necessary during precipitation.

e. If there is a colloidal suspension present, add 3 cc.  $\text{NH}_4\text{NO}_3$  solution, heat nearly to boiling and filter through the same paper that contains the main precipitate of the group.

f. Although a full description will be given later of the method of analyzing when all groups are present, it is worth while to give a warning here that the filtrate from Group II should not be set aside without first boiling down and filtering to remove any free S. Otherwise there will be formed ions of  $\text{SO}_4^{--}$  which will prematurely precipitate some of the alkaline-earth group.

g. Arsenates, antimonates and stannates are sometimes very slow of reduction, and the precipitating process must be repeated until no further precipitate is obtained by  $\text{H}_2\text{S}$ . Group II must under no circumstances be allowed to pass on to subsequent groups. This statement applies to all groups, but caution is especially necessary here because the other groups do not involve slow reduction processes such as may be required for the precipitation of the  $\text{H}_2\text{S}$  group.

h. Under no circumstances permit the strongly caustic  $(\text{NH}_4)_2\text{S}_x$  solution to come in contact with filter paper. Either scrape off the precipitate or wash



the paper with a little water in the evaporating dish. Remove the paper before adding  $\text{Na}_2\text{S}_x$ .

i. The amount of  $\text{Na}_2\text{S}_x$  to be added depends upon the amount of precipitate, and this in turn depends upon the solution which is being analyzed and the amounts of radicals present. You must understand exactly what you are doing and why you are doing it; then the number of cubic centimeters will be a matter for your judgment to decide. In this case there must surely be added about three to four times the volume of sulfide precipitate.

j. You can tell when solution is complete by the way in which the solution clears up and the manner in which the free S collects at the surface.

k. Warming will have a tendency to dissolve the mercury and put it in subdivision B. It can be taken care of there, but it is best to retain it in subdivision A as far as possible.

l. The caustic solution, unless diluted, may weaken the filter paper so much that the bottom breaks through.

m. The filtrate is considered first because upon standing it will slowly decompose and a mixture of the reprecipitated sulfides and free S will form a deposit on the walls of the containing vessel. This is difficult to remove. Frequently students pour the liquid out of the containing vessel and disregard the adhering deposit. In this case much of the subdivision may be lost. While working with subdivision B, if there is danger of subdivision A becoming dried out, it can be kept moist as described in the preliminary section on laboratory work.

n. Where much HgS is present or where the polysulfide digestion was overdone by warming the solution, quite an amount of HgS may go into subdivision B. It will not dissolve in  $(\text{NH}_4)_2\text{CO}_3$ , and consequently is found in the precipitate with  $\text{Sb}_2\text{S}_5$ ,  $\text{SnS}_2$  and S. A warning should have been obtained in the preliminary test for mercury before Group II was precipitated. The polysulfide should be kept cold and thoroughly stirred. If the digestion is carefully done with cold  $12n$  HCl, most if not all the HgS will be kept out of solution. The antimony and tin sulfides are very soluble in cold  $12n$  HCl. When only a trace of mercury goes into solution with the chlorides of antimony and tin, the final black particles of HgS will not obscure either the  $\text{Sb}_2\text{S}_5$  or the  $\text{SnS}_2$ .

o. "Leaching" is a term used to denote the process of pouring a solvent repeatedly over a solid mass to extract the soluble portion.

p. Do not attempt to get all of the residue in solution. The S certainly will not dissolve in HCl.

q. The total volume should be 65 cc. so that the acidity will permit  $\text{Sb}_2\text{S}_5$  and  $\text{Sb}_2\text{S}_3$  to precipitate in a hot solution, but the  $\text{SnS}_2$  will remain dissolved until the solution is cooled.

r. With a little practice this method of identifying antimony and tin can be made very accurate. If the tin is in large excess it may precipitate even in the hot solution and somewhat obscure the presence of antimony, but even under these conditions the red shade of the antimony sulfide should be apparent.

s. Although HgS ordinarily does not dissolve in  $\text{HNO}_3$  and frequently will not dissolve completely in aqua regia, there are other times, due evidently to a very favorable physical condition, when the precipitate will dissolve to



quite an extent in the dilute acid used here. Where mercury goes through it will appear in the final precipitation of CdS and darken it to such an extent that identification is made very difficult. A preliminary test for mercury is therefore desirable before precipitating the  $H_2S$  group. It can be made in the usual way with  $SnCl_2$  solution. If Hg is present heat must not be applied, but if it is absent the solution can be heated quite strongly and the remaining sulfides of the group will be dissolved more rapidly. A dark residue will not necessarily indicate  $HgS$ . Where the solution is warmed the free S will frequently darken in color. Where  $HgS$  is also present it may enclose the black precipitate, and the resulting mass is very difficult to break up.

t. The volume of nitrate solution and washings will usually be about 10 cc. If the volume is greater than this it shows that an excessive amount of nitric acid was used and the total volume must be reduced by boiling until it is not over 10 cc. Cultivate the habit of using the least amount of reagent that will accomplish the desired result. Large volumes mean a waste both of time and material. By using a one-third volume ratio of solution and acid, a uniform acidity will result. If we were to state that 3 cc. concentrated acid should be added to the filtrate it would not mean a thing as far as resulting acidity is concerned.

u. It was pointed out in the preliminary work that when  $HNO_3$  is present a soluble acid sulfate may result. The  $HNO_3$  can be driven off by this heating process in the presence of  $H_2SO_4$ . When  $SO_3$  fumes appear it is inferred that a condition has been reached in which the  $H_2SO_4$  is decomposing rapidly and that  $HNO_3$  has been practically eliminated.

v. Remember the caution given in elementary chemistry to dilute very concentrated  $H_2SO_4$  by pouring into water and not in the reverse order. A white precipitate present at this point may be  $(BiO)_2SO_4$ , hence the necessity of confirming the presence of lead.

w. Lead-ion must be removed as completely as possible because it will interfere with both the bismuth and cadmium tests which follow.

x. The  $BiCl_3$  which will be next formed must not come in contact with water alone, until the final test is made. These confirmatory tests for bismuth are necessary because the white precipitate may consist of other hydroxides formed when the solution was made alkaline, as  $Pb(OH)_2$  or a basic salt of lead, for example.

y. Refer to preliminary tests for details of preparation.

z. The precipitate is the same color as *K* in Plate II, but if very concentrated it will appear a dark brown.

1a. A discolored precipitate of CdS is very unsatisfactory and usually results from  $HgS$  dissolving by the original  $HNO_3$  treatment. If copper is absent a good test should have resulted with the ferrocyanide. If copper is present some attempt must be made to clear up the discolored CdS precipitate. To do this, first be certain that the  $H_2S$  precipitation is complete, but do not continue until free S appears. Filter, wash once with water and leach through with 4 cc. 6*N*  $H_2SO_4$ . Pour back several times and remember that black  $HgS$  should remain undissolved on the paper. Dilute the filtrate with an equal volume of water and reprecipitate with  $H_2S$ . The yellow CdS should now be quite free from contamination.

### PLATE III

#### FUSIONS IN THE IDENTIFICATION OF MANGANESE, ALUMINUM AND ZINC

A. A satisfactory fusion in the identification of manganese requires (a) a large excess of  $\text{Na}_2\text{CO}_3$ , (b) a few crystals of  $\text{KClO}_3$  or  $\text{KNO}_3$ , and (c) a small amount of the precipitate  $\text{Mn}(\text{OH})_3$ . These three substances are carefully mixed and gently heated at first and then strongly until a uniform melt is obtained.

B. By withdrawing the flame occasionally it is possible to inspect the fused mass and determine when there is a maximum green color due to the presence of  $\text{Na}_2\text{MnO}_4$  and  $\text{K}_2\text{MnO}_4$ . If an excess of precipitate is taken or if the amount of oxidizing agent or heating is insufficient, a black mass will result. In this situation, remove most of the black mass, which contains  $\text{MnO}_2$  or other oxides of manganese, add more  $\text{Na}_2\text{CO}_3$  and  $\text{KClO}_3$  and reheat.

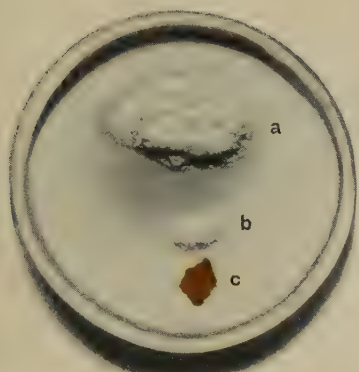
C. If the oxides are finely divided throughout an excess of fused  $\text{Na}_2\text{CO}_3$ , a gray or blue appearance often results. The same effect may be produced by the presence of cobalt compounds. More oxidizing agent should be added and the mass reheated. The green color will develop if manganese is present; cobalt compounds will not give a green fusion.

D. In B, reference was made to the necessity of removing the flame occasionally to inspect the fused mass. This photograph shows the result of following an instruction, "heat strongly." If any  $\text{Na}_2\text{MnO}_4$  ever developed, it has been decomposed and the fusion is now worthless.

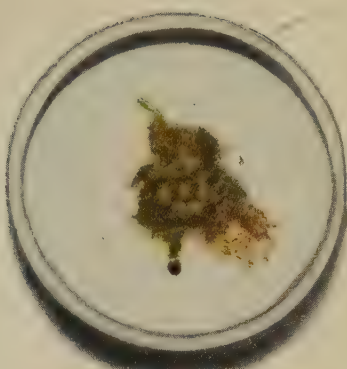
E. Thénard's Blue, Cobalt Aluminate,  $\text{Co}(\text{AlO}_2)_2$ . This blue fusion and the corresponding one of green in the test for zinc are not infrequently given incorrectly in texts. This photograph should clear up any confusion that exists as to "which is which." It should be emphasized that the fusion is made by moistening the precipitate which is being tested with a few drops of a 0.3*n* solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and then heating strongly with a gas flame. It is also desirable in this fusion to withdraw the flame occasionally to allow inspection of the mass.

F. Rinmann's Green, Cobalt Zincate,  $\text{CoZnO}_2$ . The test is made analogous to that in E.

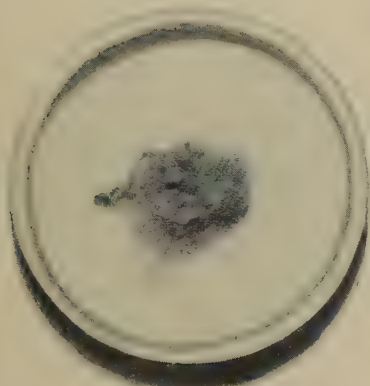
# PLATE III



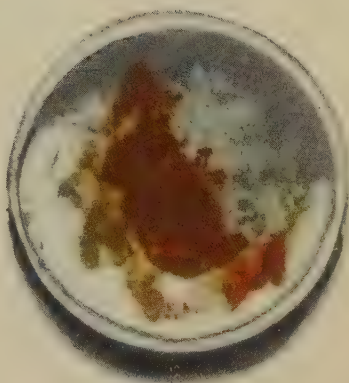
A



B



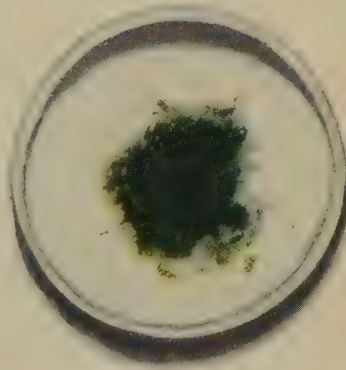
C



D



E



F



## OPTIONAL TESTS IN THE ANALYSIS OF GROUP II

The precipitation of Group II is subject to several variations but involves the three steps outlined in the summary of the reactions for this group. In one procedure 5 cc. 6*N* HCl are added to the solution for analysis, and the dilution is made to 50 cc. instead of 100 cc. at the beginning. By warming solution both higher acidity and heat are used to assist in reducing the arsenate. Subsequent cooling and dilution follow.

In another procedure the filtrate from Group I, which contains excess HCl, is first precipitated with H<sub>2</sub>S without heating or dilution. However, dilution and heating then follow. The precipitates are often filtered off as each type of precipitation is completed.

In the polysulfide separation of subdivisions A and B, (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> is frequently used in place of Na<sub>2</sub>S<sub>x</sub>. A comparison of the two reagents follows:

 Na<sub>2</sub>S<sub>x</sub>

Very stable and is easily prepared.

In a cold solution some HgS will be dissolved if there is a large amount present. In a hot solution practically all of the HgS will be dissolved; traces, however, will not be dissolved.

CuS is not dissolved except in traces.

SnS is very thoroughly oxidized and dissolved.

Some Bi<sub>2</sub>S<sub>3</sub> may be dissolved.

 (NH<sub>4</sub>)S<sub>x</sub>

Decomposes and is more difficult to prepare. Refer to Reagents in Part V.

HgS is not dissolved in either a cold or warm solution except in traces.

CuS may be dissolved to a very appreciable extent.

Small amounts of SnS will not be dissolved.

Bi<sub>2</sub>S<sub>3</sub> is not dissolved.

The sulfides of arsenic, antimony and tin are frequently separated by adding 12*N* HCl to the mixed sulfides. The Sb<sub>2</sub>S<sub>5</sub> and SnS<sub>2</sub> are dissolved and As<sub>2</sub>S<sub>5</sub> and S remain as the residue. Concentrated HNO<sub>3</sub>, or aqua regia, is used to put the As<sub>2</sub>S<sub>5</sub> into solution as H<sub>3</sub>AsO<sub>4</sub>. Arsenic is then tested for as an arsenate by the magnesia mixture in an alkaline solution, or by the ammonium molybdate reagent in a nitric acid solution.

An additional confirmatory test for Sb and Sn can be made by taking the final sulfide precipitates and dissolving them in 12*N* HCl, diluting somewhat and adding a few pieces of aluminum. If the concentration of the solution is favorable, only Sb will be precipitated. Further to identify the precipitate, the liquid can be decanted and some NaOCl solution added. Only Sn is soluble in this reagent.

Many other separations of Sb and Sn have been proposed but, as stated in the procedure, the sulfide separation in a hot solution of definite acidity will usually give satisfactory tests.

In making the sodium stannite test for bismuth the reagent can be poured



directly on the precipitate of  $\text{Bi}(\text{OH})_3$  on the filter. A black deposit of Bi results. The  $\text{Bi}(\text{OH})_3$  in this test must be well washed with hot water before the sodium stannite solution is added.

Metals are frequently introduced into the acid solution containing the nitrates of copper, bismuth and cadmium in order to test for copper. Iron, for example, may be used. Do not make this test in the main part of the solution or trouble will follow. If you care to try it, make a small side test and discard the resulting solution.

If it is desired to put all of the mercury into subdivision B, the polysulfide digestion is heated, then the solution is diluted and filtered. After reprecipitating the sulfides of mercury, arsenic, antimony and tin from the solution of the salts of the sulfacids, arsenic and mercury are separated from antimony and tin by transferring the precipitate to an evaporating dish and adding  $12n$  HCl. Under the proper conditions arsenic and mercury will remain as a residue, and by adding  $\text{NH}_4\text{OH}$  the  $\text{As}_2\text{S}_5$  will go into solution. The rest of the tests to complete this procedure have already been covered.

## PROCEDURE SHEET II

### ANALYSIS OF GROUP II

Precipitation of the Group and Separation into Subdivisions A and B.

Solution contains  $\text{Hg}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Bi}^{+3}$ ,  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{As}^{+3}$ ,  $\text{As}^{+5}$ ,  $\text{Sb}^{+3}$ ,  $\text{Sb}^{+5}$ ,  $\text{Sn}^{++}$  and  $\text{Sn}^{+4}$ . Dilute to 100 cc. in a flask and test for normality of acid with acid cresol red indicator. Adjust to make  $0.3n$  in HCl. Make preliminary tests for  $\text{Hg}^{++}$ , also  $\text{Fe}^{++}$  and  $\text{Fe}^{+3}$  where subsequent groups are present. Heat nearly to boiling and precipitate with  $\text{H}_2\text{S}$  in a stoppered flask. Cool, filter and reprecipitate filtrate if necessary. Wash total precipitate of sulfides with water containing  $\text{H}_2\text{S}$  and a few drops of  $\text{NH}_4\text{NO}_3$ .

Precipitate:  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{CdS}$ ,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_5$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_5$ ,  $\text{SnS}$ ,  $\text{SnS}_2$  and  $\text{S}$ . Digest with cold  $\text{Na}_2\text{S}_x$  if  $\text{Hg}^{++}$  is present, otherwise warm. Dilute, filter and wash with water.

Filtrate: If succeeding groups are present, boil until  $\text{H}_2\text{S}$  is removed, cool and filter if turbid and discard the free S and any Group II sulfides that may have passed through.

Residue, Subdivision A:  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{CdS}$  and  $\text{S}$ . Analyze this residue after filtrate containing Subdivision B. Keep moist by inverting in beaker containing some water.

Filtrate, Subdivision B:  $\text{Na}_3\text{AsS}_4$ ,  $\text{Na}_3\text{SbS}_4$  and  $\text{Na}_2\text{SnS}_3$ . Analyze this filtrate at once before it decomposes.

## PROCEDURE SHEET III

## ANALYSIS OF SUBDIVISION B, GROUP II

Final tests are underscored twice

This solution contains  $\text{Na}_3\text{AsS}_4$ ,  $\text{Na}_3\text{SbS}_4$  and  $\text{Na}_3\text{SnS}_3$  and is analyzed before Subdivision A on account of its instability. Add 6*N* HCl, dropwise, in slight excess and boil at intervals while the solution is being made acid. Filter, using a double filter if necessary, and wash once with hot water.

Precipitate: <u><math>\text{As}_2\text{S}_5</math>, <math>\text{Sb}_2\text{S}_5</math>, <math>\text{SnS}_2</math> and S.</u> Digest with $(\text{NH}_4)_2\text{CO}_3$ , dilute, filter and wash with water.		Filtrate: $(\text{NH}_4)_2\text{AsO}_3\text{S}$ and $(\text{NH}_4)_3\text{AsS}_4$ . Add HCl in slight excess. A light yellow ppt. of <u><math>\text{As}_2\text{S}_5</math></u> indicates arsenic. Pass $\text{H}_2\text{S}$ through the solution for a few moments to increase the precipitate if present in traces.	Filtrate: Discard unless there is a colloidal suspension. It is probably S but can be coagulated by adding $\text{NH}_4\text{NO}_3$ and boiling. Filter and combine with main ppt.	
Residue: <u><math>\text{Sb}_2\text{S}_5</math>, <math>\text{SnS}_2</math> and S.</u> Dissolve in 12 cc. 12 <i>N</i> HCl by leaching on filter paper. Wash once with water.				
Residue: S. Discard.	Filtrate: <u><math>\text{SbCl}_3</math>, <math>\text{SbCl}_5</math>, and <math>\text{SnCl}_4</math>.</u> Dilute to 65 cc., heat to boiling, ppt. with $\text{H}_2\text{S}$ and filter while hot.			
	Precipitate: Orange-red ppt. of <u><math>\text{Sb}_2\text{S}_3</math></u> and <u><math>\text{Sb}_2\text{S}_5</math></u> indicates antimony. Confirm by special optional tests if necessary.			Hot solution: $\text{SnS}_2$ . Cool and a yellow ppt. of <u><math>\text{SnS}_2</math></u> indicates tin. Confirm by special tests if necessary.

PROCEDURE SHEET IV  
ANALYSIS OF SUBDIVISION A, GROUP II

Final tests are underscored twice

This residue contains HgS, PbS, Bi<sub>2</sub>S<sub>3</sub>, CuS, CdS and S. Transfer to evaporating dish, digest with 6*n* HNO<sub>3</sub>, filter and wash once with water.

Residue: <u>HgS</u> and <u>S</u> . Digest with aqua regia for a few minutes, dilute with 10-15 cc. water. Boil until excess acid and Cl <sub>2</sub> are removed. Cool, and add SnCl <sub>2</sub> solution dropwise. A white ppt. of <u>HgCl</u> changing to a blue-black ppt. of <u>Hg</u> indicates mercuric mercury.		Filtrate: Pb(NO <sub>3</sub> ) <sub>2</sub> , Bi(NO <sub>3</sub> ) <sub>3</sub> , Cu(NO <sub>3</sub> ) <sub>2</sub> and Cd(NO <sub>3</sub> ) <sub>2</sub> . If volume is more than 10 cc., concentrate by boiling to this volume. Add conc. H <sub>2</sub> SO <sub>4</sub> equal to one-third of the volume of solution and evaporate under a hood until SO <sub>3</sub> fumes are freely evolved. Cool, dilute with 10 cc. water and decant solution through filter paper.
Precipitate: A white ppt. of PbSO <sub>4</sub> indicates lead. Confirm by dissolving in hot (NH <sub>4</sub> ) <sub>2</sub> Ac and conc. HAc. Add a few drops of K <sub>2</sub> CrO <sub>4</sub> and a yellow ppt. of PbCrO <sub>4</sub> confirms lead.	Filtrate: Bi <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , CuSO <sub>4</sub> and CdSO <sub>4</sub> . Add conc. NH <sub>4</sub> OH in excess, filter and wash ppt. with water.	
	Precipitate: Bi(OH) <sub>3</sub> . Transfer paper to a dry funnel. Add a few drops of conc. HCl and confirm bismuth by adding 2 drops of the BiCl <sub>3</sub> to (a) cold water, giving a white ppt. of BiOCl; (b) solution of Na <sub>2</sub> SnO <sub>2</sub> giving a black ppt. of Bi.	Filtrate: Cu(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup> and Cd(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup> . The blue solution of Cu(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup> indicates copper. Confirm by taking 2 cc. of solution, making acid with HAc and adding a few drops of K <sub>4</sub> [Fe(CN) <sub>6</sub> ]. A red ppt. of Cu <sub>2</sub> [Fe(CN) <sub>6</sub> ] confirms copper.  In the absence of copper, a white ppt. of Cd <sub>2</sub> [Fe(CN) <sub>6</sub> ] indicates cadmium.  Where copper is present, decolorize the ammoniacal solution by adding, dropwise, a KCN solution in slight excess. Pass H <sub>2</sub> S through the solution and a yellow ppt. of CdS confirms cadmium.

## CHAPTER V

### GROUP III.—THE AMMONIUM SULFIDE OR ALKALINE SULFIDE GROUP

NICKEL,	Ni; at. wt. 58.69; $\text{Ni}^{++}$
COBALT,	Co; at. wt. 58.94; $\text{Co}^{++}$
MANGANESE,	Mn; at. wt. 54.93; $\text{Mn}^{++}$
IRON,	Fe; at. wt. 55.84; $\text{Fe}^{++}$ and $\text{Fe}^{+3}$
ALUMINUM,	Al; at. wt. 26.97; $\text{Al}^{+3}$
CHROMIUM,	Cr; at. wt. 52.01; $\text{Cr}^{+3}$
ZINC,	Zn; at. wt. 65.38. $\text{Zn}^{++}$

This group consists of cations which were not precipitated in Group I and whose sulfides are not precipitated in a solution which has an acidity of  $0.3n$  HCl. They are precipitated, however, in an ammoniacal solution containing  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{S}$ .

#### PRELIMINARY TESTS

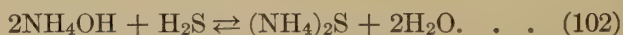
##### NICKEL-ION, $\text{Ni}^{++}$ (GREEN)

It may seem a little odd that  $\text{Ni}^{++}$  will be considered almost to the exclusion of  $\text{Ni}^{+3}$ . We might naturally expect  $\text{Ni}^{+3}$  to be the more common. With  $\text{Sn}^{++}$  and  $\text{Cu}^+$  the tendency is to change to the "ic" condition, while with nickel, the "ous" salts are so stable that only by the use of rather strong oxidizing agents is the higher valence developed. We shall therefore use nickelous salts and have nickelous compounds result under ordinary reacting conditions.

**1. Nickelous Sulfide,  $\text{NiS}$ .**—Take 5 cc. test solution of  $\text{NiCl}_2$ , add 5 cc.  $6n$  HCl, dilute with 100 cc. water and pass  $\text{H}_2\text{S}$  through for three minutes. Is there a precipitate? Show how this explains the non-precipitation of  $\text{NiS}$  in Group II. Even strong acetic acid will prevent the precipitation of  $\text{NiS}$ .

Take another 5-cc. portion of  $\text{NiCl}_2$  solution, dilute with 100 cc. water and add, dropwise,  $\text{NH}_4\text{OH}$  until just alkaline (use litmus paper) and then add 2 cc. in excess. Disregard any green precipitate or turbidity which may form because of the presence of  $\text{Ni}(\text{OH})_2$  or basic salts. Now pass  $\text{H}_2\text{S}$  through. Write the equation for the reaction. What is the color of the precipitate? Try to filter a portion of it. The colloidal tendency of  $\text{NiS}$  is quite characteristic and differs in this respect from  $\text{CoS}$ . If the colloidal  $\text{NiS}$  did not form, take some of the solution and precipitate and pass an excess of  $\text{H}_2\text{S}$  through. An excess of reagent usually brings about the colloidal condition of  $\text{NiS}$ . Add 1 cc. acetic acid to the solution containing the  $\text{NiS}$  suspension. Boil and, after coagulation has taken place, filter and wash with water containing a little  $\text{H}_2\text{S}$ . The  $\text{H}_2\text{S}$  in the wash water will prevent the formation of soluble  $\text{NiSO}_4$ .

The precipitating reagent for the Group III sulfides consists of  $(\text{NH}_4)_2\text{S}$  as shown by the following:



Remember that only the alkali sulfides are soluble in water.

Test the solubility of  $\text{NiS}$  in  $\text{NH}_4\text{Cl}$  by taking a small amount of the precipitate in a test tube and adding  $3n$   $\text{NH}_4\text{Cl}$ , 1 cc. at a time. Warm after each addition. Refer now to the equation where  $\text{NiS}$  is precipitated from a solution of  $\text{NiCl}_2$  by  $(\text{NH}_4)_2\text{S}$  and decide whether precipitation can take place in the presence of much  $\text{NH}_4\text{Cl}$ .

To another portion of  $\text{NiS}$  in an evaporating dish add 10 cc.  $2n$   $\text{HCl}$ . Stir at intervals but do not warm. At the end of ten minutes, filter and test the filtrate for the presence of  $\text{NiCl}_2$  by neutralizing with  $\text{NH}_4\text{OH}$  and passing through  $\text{H}_2\text{S}$ . Remember that this is a very delicate test for the presence of  $\text{Ni}^{++}$ . Did the precipitate of  $\text{NiS}$  appear to have dissolved to any great extent? Place the filter paper containing the  $\text{NiS}$  in an evaporating dish and cover with  $2n$   $\text{HCl}$  and allow it to stand for several hours; then decant some of the liquid and test for the presence of  $\text{NiCl}_2$ . Later we shall separate  $\text{Ni}$  from other radicals by adding  $2n$   $\text{HCl}$ . The time of contact with the acid must be limited or  $\text{NiS}$  will also go into solution as we have just seen. Reference was made in the



section on solution to the fact that ultimate solubility and rate of solubility must both be considered in making separations. Test the solubility of NiS in aqua regia. The reaction is:

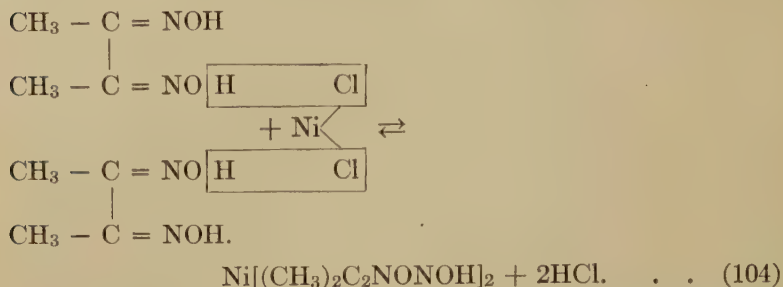


A dark precipitate which will not dissolve is often present. This consists of S that has become dark and of a gummy nature, and it frequently incloses some NiS and also prevents its solution. The sulfide is also soluble in strong  $\text{HNO}_3$  but does not dissolve as rapidly as in the aqua regia.

**2. Nickelous Hydroxide,  $\text{Ni}(\text{OH})_2$ , and Nickelic Hydroxide,  $\text{Ni}(\text{OH})_3$ .**—Add NaOH to a solution of  $\text{NiCl}_2$ . Describe the precipitate. Is it soluble in an excess of reagent? What does this show? Filter and note whether the color of the precipitate changes in the air. Place some of the precipitate in a test tube, add a little water and stir to break up the solid. Now add 3 drops NaOH solution and 1 cc. bromine water and warm. The black precipitate is largely  $\text{Ni}(\text{OH})_3$ . Take 5 cc. test solution of  $\text{NiCl}_2$  and add 5 cc. water and  $\text{NH}_4\text{OH}$  just in excess. Add to this 2 cc.  $3n \text{NH}_4\text{Cl}$  and an excess of concentrated  $\text{NH}_4\text{OH}$  until a blue solution results. Nickel complexes are formed under these conditions as  $\text{Ni}(\text{NH}_3)_4^{++}$  and  $\text{Ni}(\text{NH}_3)_6^{++}$ . This should emphasize the fact that nickel cannot be precipitated by ammonia in the presence of much ammonium salt.

**3. Nickel Dimethyl Glyoxime,  $\text{Ni}[(\text{CH}_3)_2\text{C}_2\text{NONOH}]_2$ .**—Dilute 1 cc.  $\text{Ni}(\text{NO}_3)_2$  test solution with 10 cc. water, make alkaline with  $\text{NH}_4\text{OH}$  in slight excess and disregard any precipitate that forms. Add a few drops of dimethyl glyoxime reagent and mix thoroughly. A red coloration or precipitate should appear. This can be concentrated by adding 3–4 cc. ether, closing the end of the test tube with the thumb and inverting about four times to insure thorough mixing. Do not shake, as the ether will be volatilized to a large extent. Allow the liquids to settle and note the concentration of color in the upper ether layer. It is not necessary to obtain a red or brown precipitate. If the concentration is not sufficient to exceed the  $K_{\text{SP}}$ , a red solution of the dissolved molecules will result. Refer to Plate V, A. If the solutions are quite concentrated the precipitate may be brown instead of red. The structural formula will show how the reaction occurs. The

H of the NOH group has acid properties and the resulting compound is an acid salt



Why was the solution made alkaline? Determine experimentally if your answer is correct.

**4. Potassium Nickelous Nitrite,  $\text{K}_4[\text{Ni}(\text{NO}_2)_6]$ .**—Take 5 cc. test solution of  $\text{NiCl}_2$ , add a few drops of acetic acid, a few crystals of  $\text{KCl}$  and 5 cc.  $\text{KNO}_2$  solution. Warm for ten minutes and set aside. Is a precipitate formed? Compare in the next section with a similar cobalt reaction. Nickel is not oxidized as readily as cobalt, and this difference is often used in separating the radicals.

**5. Additional Precipitates of Nickelous-ion.**—Nickelous cyanide,  $\text{Ni}(\text{CN})_2$ , green, readily soluble in excess.

**6. Borax Bead Test.**—Make a borax bead test by evaporating a few drops of a nickel test solution to dryness and touching the hot borax bead to a few particles of the solid, and then reheating in an oxidizing flame (see Plate VI and compare color of bead with *M* and *T*). Evaporate a few drops of nickel solution to which 3 drops of cobalt solution have been added. Make another bead test and decide whether the nickel bead test is conclusive in the presence of cobalt salts.

### EXERCISES

1. Has  $\text{Ni}(\text{OH})_2$  acid properties?
2. How would you determine experimentally whether the nickel ammonia complexes are very unstable?
3. How do you account for the fact that in the  $\text{H}_2\text{S}$  group precipitation  $0.3n$   $\text{HCl}$  prevents the precipitation of  $\text{NiS}$  but that later we can separate  $\text{NiS}$  as a residue from  $\text{ZnS}$  by using  $n$   $\text{HCl}$  as the solvent?
4. Write the reaction for the oxidation of  $\text{Ni}(\text{OH})_2$  to  $\text{Ni}(\text{OH})_3$  by bromine water. Why should the solution be alkaline before the bromine water is added?
5. Write the equation for the formation of  $\text{K}_4[\text{Ni}(\text{NO}_2)_6]$  from  $\text{NiCl}_2$ ,  $\text{KCl}$ , a large excess of  $\text{KNO}_2$  and acetic acid.

COBALT-ION,  $\text{Co}^{++}$  (PINK)

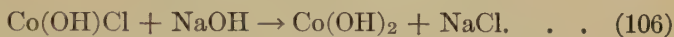
Since the reactions of  $\text{Co}^{++}$  are somewhat analogous to those of  $\text{Ni}^{++}$  we must note very carefully any distinctions which may be made so that they can be used later in the separation of cobalt and nickel. As with nickel, we shall use the "ous" salts.

**1. Cobaltous Sulfide,  $\text{CoS}$ .**—Can  $\text{CoS}$  be precipitated in the presence of  $0.3n$   $\text{HCl}$ ? Pass  $\text{H}_2\text{S}$  through an ammoniacal solution of  $\text{CoCl}_2$  and see whether  $\text{CoS}$  has the same tendency to form the colloidal state as we found with  $\text{NiS}$ . Is  $\text{CoS}$  soluble in an excess of  $(\text{NH}_4)_2\text{S}$ ? How does this compare with  $\text{NiS}$ ? Filter and wash the precipitate of  $\text{CoS}$ . What is its color? Test its solubility in  $\text{NH}_4\text{Cl}$ ,  $2n$   $\text{HCl}$  and aqua regia as you did with  $\text{NiS}$ . Give the results. Can  $\text{CoS}$  and  $\text{NiS}$  be separated by any solubility tests made so far?

**2. Cobaltous Hydroxide,  $\text{Co}(\text{OH})_2$ .**—Place 5 cc. test solution of  $\text{CoCl}_2$  in a 200-cc. flask, dilute with 10 cc. water and add  $\text{NaOH}$  solution, dropwise, until precipitation is complete. The precipitate is blue and the reaction is shown in the following:



What is the name of the precipitate? Warm the flask and note how the blue color of the precipitate changes to pink, or red. The reaction is:



Filter and wash. Test the solubility of some of the cobaltous hydroxide in an excess of  $\text{NaOH}$ . What does the result show? Place some of the precipitate on a sheet of paper and expose to the air. The black substance formed by oxidation is  $\text{Co}(\text{OH})_3$ .

Start with another portion of cobalt test solution and add  $\text{NH}_4\text{OH}$  in slight excess.  $\text{Co}(\text{OH})\text{Cl}$  should be formed as with the  $\text{NaOH}$ . Now add concentrated  $\text{NH}_4\text{OH}$  until the solution has turned brown. Warm until a reddish solution of cobalt complexes results. Test the instability of the complexes by passing  $\text{H}_2\text{S}$  through the solution. It may be necessary to dilute the solution a little. Why?

Repeat the experiment and add some  $\text{NH}_4\text{Cl}$  solution before the  $\text{NH}_4\text{OH}$  is added in excess. Does the presence of the ammonium salt promote the formation of the ammonia complex?

**3. Cobalt Salts Do Not Give a Precipitate with Dimethyl Glyoxime.**—Compare with a similar test with nickel salts.

**4. Potassium Cobaltinitrite,  $K_3[Co(NO_2)_6]$ .**—Make potassium cobaltinitrite in a manner analogous to that outlined in "4" of nickel-ion tests. The yellow precipitate resulting gives a method for the identification of cobalt in the presence of nickel.

**5. Cobalti-nitroso- $\beta$ -naphthol,  $Co[C_{10}H_6(NO)O]_3$ .**—This bluish-red precipitate is very characteristic of  $Co^{++}$  and is made by adding  $\alpha$ -nitroso- $\beta$ -naphthol,  $C_{10}H_6(NO)OH$  to a cold, slightly acid solution of a cobaltous salt. No similar precipitate is formed with  $Ni^{++}$  unless the solution is very concentrated. The solution can be warmed to hasten precipitation.

**6. Additional Precipitate of Cobalt-ion.**—Cobaltous cyanide,  $Co(CN)_2$ , light brown, soluble in excess of  $KCN$ .

**7. Borax Bead Test.**—Evaporate a few drops of cobalt solution to dryness and make a borax bead test in the oxidizing flame. Compare with Plate VI, *K* and *P*.

Devise your own method to determine whether the bead test for cobalt can be made in the presence of nickel.

### EXERCISES

1. Prepare in tabulated form a list of the precipitates of cobalt and nickel so far studied and contrast their solubilities in the solvents which we have used.

2. If cobalt and nickel nitrates are in the same solution, devise several methods for separating  $Co^{++}$  from  $Ni^{++}$ .

3. The properties of cobalt and nickel are very similar. Locate the elements in the periodic classification.

### MANGANESE-ION, $Mn^{++}$ (COLORLESS)<sup>1</sup>

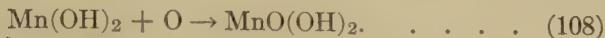
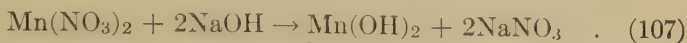
The element manganese with its plus valences of 2, 3, 4, 6, and 7, is a striking example of an element showing a gradation of properties with valence changes. The properties change from basic in  $Mn^{++}$  to strongly acidic in  $Mn^{+7}$ .

The transition from metallic to non-metallic radical occurs in going from a valence of +3 to +4. Which valence is used in the periodic classification? Which valence or valences will manganese have in the most stable series of salts?

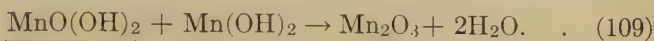
<sup>1</sup>  $MnCl_2 \cdot 4H_2O$  and  $MnSO_4 \cdot 7H_2O$  form crystals with a pale pink color. The solutions of these salts are also pink, but Talbot and Blanchard in "Electrolytic Dissociation Theory," page 66, state that the ion is colorless.



**1. Manganous Hydroxide,  $\text{Mn}(\text{OH})_2$ .**—Add  $\text{NaOH}$  to a test solution of  $\text{Mn}(\text{NO}_3)_2$  in a flask until precipitation is complete. The white precipitate of  $\text{Mn}(\text{OH})_2$  is first formed, and this changes to brown  $\text{MnO}(\text{OH})_2$  as shown in the following:



The precipitate of  $\text{MnO}(\text{OH})_2$  should not be permitted to dry in the air because it will finally change to  $\text{Mn}_2\text{O}_3$ , as shown by:

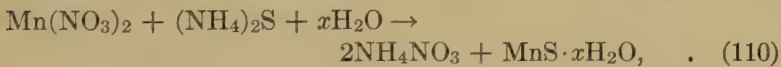


Determine whether the hydroxides are soluble in excess of  $\text{NaOH}$ . What does this indicate?

Precipitate a test solution of  $\text{Mn}(\text{NO}_3)_2$  with  $\text{NH}_4\text{OH}$ . Do you have the same color changes as when  $\text{NaOH}$  was used? Does manganese form ammonia complexes? Devise your own experiment to answer this question.

Using another portion of a test solution of  $\text{Mn}(\text{NO}_3)_2$ , add  $\text{NH}_4\text{Cl}$  before the  $\text{NH}_4\text{OH}$ . Test with litmus to make sure that the solution has been made alkaline. A precipitate should not form at once, but finally brown  $\text{Mn}_2\text{O}_3$  will appear. If you use ammonium salts to prevent the precipitation of manganese hydroxide in the presence of other hydroxides, show how the last test emphasized the necessity of filtering immediately after the hydroxide reagent is added to the solution which is being precipitated. Test the solubility of the hydroxides of manganese in  $n$   $\text{HCl}$ .

**2. Manganous Sulfide,  $\text{MnS}$ .**—Precipitate  $\text{MnS}$  from a test solution of  $\text{Mn}(\text{NO}_3)_2$  by first making ammoniacal and then passing  $\text{H}_2\text{S}$  through. First there is formed a pink hydrated sulfide which changes on boiling into a less hydrated green sulfide, as shown by:



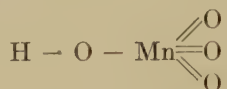
Test the solubility of a precipitate of these sulfides in  $2n$   $\text{HCl}$  and  $6n$  acetic acid.

**3. Sodium Manganate,  $\text{Na}_2\text{MnO}_4$ .**—Add  $\text{Na}_2\text{CO}_3$  and solid  $\text{KClO}_3$  to a precipitate of the hydroxides of manganese and fuse

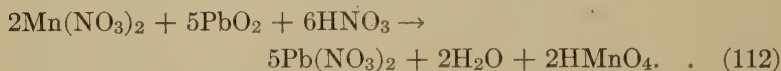


on a porcelain crucible cover or in a bead. Green  $\text{Na}_2\text{MnO}_4$  and  $\text{K}_2\text{MnO}_4$  result. Explain the reactions involved (see Plate III for a discussion of manganese fusions, also Plate VI, *F* and *G* for the fusion in bead form).

**4. Permanganic Acid,  $\text{HMnO}_4$ .**—Put 5 cc. 12*n*  $\text{HNO}_3$ , in a test tube and add a few crystals of a manganous salt and 1 gram  $\text{PbO}_2$ . Heat nearly to boiling and until a reddish-violet color develops in the supernatant liquid. The color is more noticeable after the solids have been allowed to settle (see Plate V, *D*). The structural formula of the acid is:



What is the valence of Mn here? The color of the solution is due to  $\text{MnO}_4^-$  and not to the molecule. The reaction is:



**5. Bead Tests.**—The sodium carbonate bead test was considered in “3” of this section in connection with  $\text{Na}_2\text{MnO}_4$ . A borax bead with manganese compounds, particularly with a manganate, gives a characteristic “amethyst” color (see Plate VI, *H* and *O*).

### EXERCISES

1.  $\text{MnO}(\text{OH})_2$  is manganous acid. Write the structural formula. What is the characteristic name of salts of this acid? Do they exist? (Even the manganates are unstable in solution.)

2. If the hydroxides of manganese are dissolved in *n*  $\text{HCl}$  and then  $\text{Na}_2\text{O}_2$  is added in excess, will the precipitate first formed redissolve? Why?

3. Balance by the electron-transfer method the equation given for the oxidation of a manganous salt to permanganic acid.

4. Compare the solubilities of  $\text{CoS}$ ,  $\text{NiS}$  and  $\text{MnS}$  in *n*  $\text{HCl}$ ; in acetic acid.

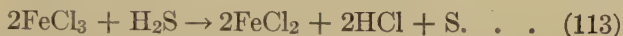
### FERROUS-ION, $\text{Fe}^{++}$ (PALE GREEN)

Both ferrous and ferric salts are used in qualitative analysis and the corresponding ions are therefore considered.  $\text{Fe}^{++}$  very readily changes to  $\text{Fe}^{+3}$ , even in the presence of air as the oxidizing agent. Ferrous salts are therefore very unstable. A freshly prepared solution of ferrous-ammonium sulfate,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ ,

is a convenient source of  $\text{Fe}^{++}$ . What type of compound is ferrous-ammonium sulfate? Are the properties of  $\text{Fe}^{++}$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{--}$  present in a solution of this substance?

**1. Ferrous Sulfide,  $\text{FeS}$ .**—Take 5 cc. test solution of ferrous-ammonium sulfate, add 5 cc.  $6n$   $\text{HCl}$ , dilute with 100 cc. water and pass through  $\text{H}_2\text{S}$ . Give result and explain. Using the same amount of test solution and water as before, make alkaline with  $\text{NH}_4\text{OH}$  and pass  $\text{H}_2\text{S}$  through. What is the first precipitate which forms? If very dark brown or black  $\text{FeS}$  is the final precipitate how do you explain the change? Filter and wash with water containing  $(\text{NH}_4)_2\text{S}$ . What is the purpose of adding  $(\text{NH}_4)_2\text{S}$  to the water? Should the filtering be done immediately? Test the solubility of  $\text{FeS}$  in a large excess of  $\text{NH}_4\text{OH}$  and in  $2n$   $\text{HCl}$  and in  $\text{NaOH}$ . What can be concluded? Upon standing in air, will ferrous sulfide oxidize to ferric sulfate?

Take a dilute solution of ferric chloride and test with litmus paper. Why is the solution acid? Add a few drops more  $\text{HCl}$  and pass  $\text{H}_2\text{S}$  through until the solution has changed from a light yellow to colorless. The equation is:



Will the  $\text{FeCl}_2$  be precipitated as  $\text{FeS}$  in the acid solution?

**2. Ferrous Hydroxide,  $\text{Fe}(\text{OH})_2$ .**—Precipitate  $\text{Fe}(\text{OH})_2$  by adding  $\text{NH}_4\text{OH}$  in excess to a solution of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ . Filter and decide whether some of the precipitate is in colloidal suspension. How does the precipitate on the paper change in color? The first precipitate which forms should be a dull white gelatinous precipitate of  $\text{Fe}(\text{OH})_2$  which changes to a dirty green and finally to the reddish-brown of  $\text{Fe}(\text{OH})_3$  (see Plate II, K). The precipitate contains throughout these transformations various combinations of oxides and hydrated oxides. There is some question even in the case of  $\text{Fe}(\text{OH})_3$  as to whether it is a true hydroxide or hydrated  $\text{Fe}_2\text{O}_3$ .

Precipitate more  $\text{Fe}(\text{OH})_2$ , this time using  $\text{NaOH}$  as the reagent. Do the results differ from those where  $\text{NH}_4\text{OH}$  was used? Filter quickly and test the solubility of the precipitate in  $2n$   $\text{HCl}$  and acetic acid.

Start with another 5 cc. test solution of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ , add 10 cc.  $4n$   $\text{NH}_4\text{Cl}$ , make alkaline with  $\text{NH}_4\text{OH}$  and pass  $\text{H}_2\text{S}$  through. Is there any precipitate? Explain.

**3. Ferrous Ferricyanide,  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ .**—Dilute 1 cc. ferrous-ammonium sulfate solution with 100 cc. water and add a few drops of potassium ferricyanide. The blue precipitate,  $\text{Fe}_3[\text{Fe}(\text{CN})_6]$ , is ferrous ferri(c)-cyanide, or Turnbull's blue (see Plate II, *O*). Write the equation. Filter, and notice if there is any tendency to form a colloidal suspension. Add, to small portions of the precipitate, acetic acid, *n* HCl and NaOH. Give the results and an explanation in each case. Pour a few drops of oxalic acid solution through the precipitate. What is the result? Could the precipitate be formed in the presence of this organic substance?

**4. Ferrous Ferro(us) Cyanide,  $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ .**—Boil about 5 cc. water in a test tube for two minutes and stopper the tube loosely with a plug of cotton. Cool with tap water and carefully introduce, without admitting air currents, two small crystals of a ferrous salt and 3 drops of potassium ferrocyanide,  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . If the air has been well excluded, a white precipitate of ferrous ferrocyanide,  $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ , will form. It will probably change quite rapidly to the blue ferric compound, so the original precipitate may not be entirely white. Test the solubility of this precipitate in HCl by adding HCl to the solution in the test tube.

**5. Ferrous Thiocyanate,  $\text{Fe}(\text{SCN})_2$ .**—Place about  $\frac{1}{2}$  inch of fine iron wire in a test tube and cover with 5 cc. 6*n* HCl. If the action does not start soon, warm and add a few drops of concentrated acid. Stopper loosely with a cotton plug. When the evolution of gas has ceased, introduce a few drops of KSCN or  $\text{NH}_4\text{SCN}$ . Is there a precipitate or color change in the solution? Write an equation for the reaction of iron and hydrochloric acid. Since the red color of  $\text{Fe}(\text{SCN})_3$  is an extremely delicate test for  $\text{Fe}^{+3}$ , the precautions taken in this test can readily be appreciated. There is no color change when  $\text{Fe}^{++}$  and SCN are combined.

**6. Oxidation of Ferrous to Ferric Salts.**—Although ferrous compounds readily oxidize to ferric in the air, try the effect of an oxidizing agent upon a ferrous salt solution. Will bromine water be a good selection?

**7. Additional Precipitate of Ferrous-ion.**—Ferrous cyanide,  $\text{Fe}(\text{CN})_2$ , brown, soluble in excess of KCN.

**8. Bead tests** are given in connection with ferric-ion.

## EXERCISES

1. Give several examples where the presence of ammonium salts has prevented the formation of a precipitate.

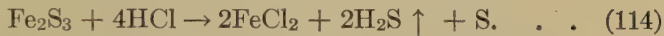
2. Make a list of oxidizing agents that might be used to oxidize ferrous compounds to ferric. Write two equations to show the reactions of two of the oxidizing agents on ferrous compounds.

3. What will be the valence of the iron contained in the filtrate from Group II? What objections are there to precipitating ferrous compounds in the Group III precipitate?

4. Give several reducing agents that might be used to reduce  $\text{FeCl}_3$  to  $\text{FeCl}_2$ . Write the equation for one of the reductions.

FERRIC-ION,  $\text{Fe}^{+3}$  (COLORLESS)<sup>2</sup>

1. **Ferric Sulfide,  $\text{Fe}_2\text{S}_3$ .**—We have found that neither  $\text{Fe}_2\text{S}_3$  or  $\text{FeS}$  are precipitated by  $\text{H}_2\text{S}$  in acid solution. Add  $(\text{NH}_4)_2\text{S}$  to a solution of  $\text{FeCl}_3$  until it becomes alkaline. Does a precipitate form before the solution has become alkaline? Why? The final precipitate is black  $\text{Fe}_2\text{S}_3$ . Determine whether the presence of ammonium salts will prevent precipitation. Filter and dissolve some of the precipitate in  $\text{HCl}$ . The reaction is:



Does  $\text{HCl}$  react as an oxidizing or a reducing agent in this reaction? Have we had another example of a sulfide dissolving in  $\text{HCl}$  with a simultaneous reduction?

2. **Ferric Hydroxide,  $\text{Fe}(\text{OH})_3$ .**—Precipitate  $\text{Fe}(\text{OH})_3$  by adding  $\text{NaOH}$  to a solution of  $\text{FeCl}_3$ . Does it dissolve in an excess? Conclusion? Repeat, using  $\text{NH}_4\text{OH}$  as the precipitating agent. Does  $\text{Fe}^{+3}$  form ammonia complexes? See if the presence of ammonium salts prevents the precipitation of the hydroxides. Test the solubility of the precipitate in  $2n$   $\text{HCl}$  and in acetic acid. Heat some  $\text{Fe}(\text{OH})_3$  on a porcelain crucible cover. The black residue is  $\text{Fe}_2\text{O}_3$ . Will  $6n$   $\text{HCl}$  dissolve it readily? Remember that evaporating a solution about to dryness does not mean to drive off all of the fluid and then heat the residue without limit.

<sup>2</sup> A solution of  $\text{FeCl}_3$  is yellow or a light amber because of the presence of undissociated molecules of  $\text{FeCl}_3$  and is, of course, acid with  $\text{HCl}$  to prevent hydrolysis. If the solution is almost neutral, a reddish-brown color may develop, due to the formation of a trace of  $\text{Fe}(\text{OH})_3$  by hydrolysis. Ferric-ion, however, is colorless.



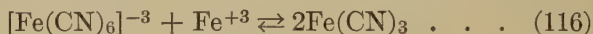
Not only will volatile compounds be lost but others may be changed in such a way that subsequent solution is very difficult.

**3. Ferric Ferrocyanide,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ .**—Add a few drops of potassium ferrocyanide to a dilute solution of  $\text{FeCl}_3$ . The blue precipitate, Prussian blue (see Plate II, *P*) results as follows:



Take 2 cc. of the solution together with some of the precipitate and add the reagent in large excess. Does the precipitate tend to redissolve? Test the solubility also in 6*n* HCl, acetic acid and oxalic acid. How could you determine whether oxalic acid produces a true solution or a colloidal suspension?

**4. Ferric Ferricyanide,  $\text{Fe}[\text{Fe}(\text{CN})_6]$ .**—Add potassium ferricyanide to a dilute solution of ferric chloride. Is there a precipitate? The solution is usually brown but may have a distinct greenish shade and it undoubtedly contains more than one complex. One possible reaction is:



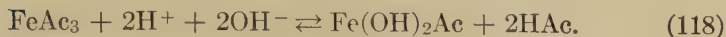
**5. Ferric Thiocyanate,  $\text{Fe}(\text{SCN})_3$ .**—Add 4 drops KSCN or  $\text{NH}_4\text{SCN}$  to 1 cc. of *n*  $\text{FeCl}_3$  which has been diluted to 100 cc. with water. The red color is due to the presence of red molecules of  $\text{Fe}(\text{SCN})_3$  (see Plate I, *A*). Warm slightly to see if the color disappears. To show how delicate the test is for  $\text{Fe}^{+3}$ , take 1 cc. of this resulting solution in a test tube, add 9 cc. water and by looking down through the test tube determine if the color is still present. A tube containing water alone can be used as a basis for comparison. Repeat this method of diluting 1 cc. and adding 9 cc. water until the color has disappeared. Now calculate the normality of the solution that gave the last distinct color.

Nitrate ions must not be present when this test is made. Take a test tube one-third full of water, add a few drops of  $\text{NH}_4\text{SCN}$  and 15 drops of concentrated  $\text{HNO}_3$ . Warm. If a red color has not appeared before, it will do so now. This is an exact color duplicate of the iron test. Finally, a decomposition begins at the top of the solution and progresses downward. The color of the solution finally becomes green (see Plate I, *F*).

**6. Basic Ferric Acetate,  $\text{Fe}(\text{OH})_2\text{Ac}$ .**—Add a solution of sodium acetate to a test solution of ferric chloride. Heat and add more



water if necessary to produce a voluminous precipitate. The reactions are:



What is the effect of increasing  $[\text{H}^+]$ ?

**7. Additional Precipitate of Ferric-ion.**—Ferric phosphate,  $\text{FePO}_4$ , light yellow.

**8. Bead Tests.**—The bead test is not very satisfactory, because of the formation of several products either in the reducing or oxidizing flame. The color is also determined to quite an extent by the salt used. The usual descriptions of the test state that in the oxidizing flame the color may be yellow when hot and yellow or colorless when cold. It will be found, however, that frequently a brown color, like that in the nickel test, results. See Plate VI, *N*. The color may be as dark as *M*. The light yellow of the hot bead is shown in *S*. In the reducing flame the color depends upon the amount of reduction that has taken place as well as the salt used. The color in *U* shows one possibility. The bead may have more of a greenish cast or even a reddish-brown.

Suggestion: Don't test for iron by the borax bead method.

### EXERCISES

1. Write the equation for the solution of  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  in a large excess of  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

2. Ferric ferrocyanide will decompose in  $\text{KOH}$ . Write the equation.

3. Show by the necessary equilibria how the  $[\text{Fe}^{+3}]$  can be determined in Exercise 2 when the reaction is in equilibrium.

4. Is ferric cyanide a possible compound? Discuss.

5. Summarize the tests that can be used to distinguish  $\text{Fe}^{++}$  from  $\text{Fe}^{+3}$ .

6. Discuss the possibility of precipitating  $\text{Fe}^\circ$  from solution by means of other metals.

7. When a solution of a ferric salt is added to a suspension of  $\text{BaCO}_3$ , a precipitate of  $\text{Fe}(\text{OH})_3$  and not  $\text{Fe}_2(\text{CO}_3)_3$  results. Explain. (SUGGESTION: The ferric salt under these conditions hydrolyzes appreciably. The action of  $\text{HCl}$ , one of the products, on  $\text{BaCO}_3$  causes  $\text{H}_2\text{CO}_3$  to be formed. Is it possible, therefore, for  $K_{\text{SP}}$  of  $\text{Fe}_2(\text{CO}_3)_3$  to be exceeded before that of  $\text{Fe}(\text{OH})_3$ ?)

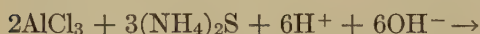
8. Show the ionic equilibria that are necessary to explain how  $\text{Fe}_2\text{S}_3$  dissolves in  $\text{HCl}$ .

ALUMINUM-ION,  $\text{Al}^{+3}$  (COLORLESS)

**1. Aluminum Hydroxide,  $\text{Al}(\text{OH})_3$ .**—Add  $\text{NH}_4\text{OH}$  to a test solution of  $\text{Al}(\text{NO}_3)_3$ . Describe the precipitate. Does it dissolve in an excess of reagent? Filter and look down through the filtrate in a test tube to determine any turbidity.  $\text{Al}^{+3}$  does not form ammonia complexes, but the hydroxide in the presence of excess  $\text{NH}_4\text{OH}$  and in the absence of neutral salts is partially dispersed into the colloidal state.

Repeat the experiment using  $\text{NaOH}$  in place of  $\text{NH}_4\text{OH}$ . Does the precipitate dissolve in an excess? Explain. Gradually neutralize the alkaline solution with  $\text{HCl}$ . Describe what happens. Now make the solution strongly acid with  $\text{HCl}$ . Give the results. Review the section in Part I that deals with amphoteric hydroxides, and write both sets of equations representing the solution of  $\text{Al}(\text{OH})_3$ . Will  $\text{Al}(\text{OH})_3$  dissolve in acetic acid or  $2n$   $\text{HCl}$ ?

$\text{Al}(\text{OH})_3$ , and not  $\text{Al}_2\text{S}_3$ , is precipitated when  $(\text{NH}_4)_2\text{S}$  is added to a solution containing  $\text{Al}^{+3}$ . Do the experiment and use solutions of  $\text{AlCl}_3$  and  $(\text{NH}_4)_2\text{S}$ . The result of the reaction is summarized by:



The final precipitate of  $\text{Al}(\text{OH})_3$  is frequently accounted for by assuming that  $\text{Al}_2\text{S}_3$  is the first product and that it is subsequently changed by hydrolysis into  $\text{Al}(\text{OH})_3$ . If we start with  $\text{AlCl}_3$  the reactions are:



The formation of  $\text{Al}_2\text{S}_3$  in any appreciable amount is very improbable. When  $\text{H}_2\text{S}$  is passed through a suspension of  $\text{Al}(\text{OH})_3$ , the latter will not be changed to the sulfide. The more logical explanation considers the ions present in solution,  $\text{Al}^{+3}$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{S}^{=}$ ,  $\text{H}^+$  and  $\text{OH}^-$ . The solubility product of  $[\text{Al}^{+3}][\text{OH}^-]^3$  is exceedingly small and, furthermore, is the smallest

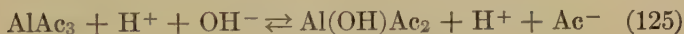
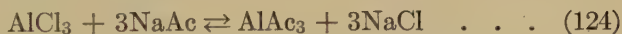
of any combination of ions present. The  $\text{Al}(\text{OH})_3$  is therefore precipitated. Review the section in Part I on hydrolysis.

$\text{Al}(\text{OH})_3$ , and not  $\text{Al}_2(\text{CO}_3)_3$ , is also precipitated when a soluble carbonate is added to a soluble aluminum salt. Select your own materials and perform the experiment. Determine whether the presence of a large excess of ammonium salts can prevent the formation of  $\text{Al}(\text{OH})_3$  in the last experiment.

Take some of the gelatinous precipitate of  $\text{Al}(\text{OH})_3$  from any of the preceding tests, dilute slightly with water and notice how the pasty particles stick to the walls of the test tube when its contents are shaken. This is very characteristic of the precipitate.

On account of the transparency of aluminum hydroxide, its presence in a solution can be made more noticeable by adding a few drops of a dye that is strongly adsorbed by the gelatinous particles. A solution of alizarin or of "Aluminon" is frequently used, and the test is made in a solution slightly alkaline with  $\text{NH}_4\text{OH}$ .

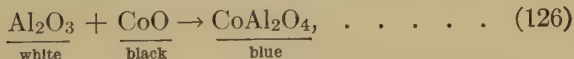
**2. Basic Aluminum Acetate,  $\text{Al}(\text{OH})\text{Ac}_2$ .**—Add a solution of sodium acetate to a test solution of aluminum chloride. Boil, and, if there is a slight precipitate only, add water and boil again. The reactions are:



What are the characteristics of this basic acetate precipitate?

**3. Aluminum Phosphate,  $\text{AlPO}_4$ .**—Add a solution of a soluble phosphate, as  $\text{Na}_2\text{HPO}_4$ , to a test solution of aluminum. Give the characteristics of the precipitate. Test the solubility in  $\text{HCl}$ ,  $\text{NaOH}$  and acetic acid.

**4. Thénard's Blue,  $\text{CoAl}_2\text{O}_4$ .**—From the reaction,



it can be seen that the blue substance results from the combination of two oxides, and it is very necessary not to have an excess of black  $\text{CoO}$  because the blue color will then be obscured. Another difficulty that may arise in the use of excess reagent is that by insufficient heating the  $\text{Co}(\text{NO}_3)_2$  may only be dehydrated and no real fusion may result. The dehydrated salt is also blue. Filter some  $\text{Al}(\text{OH})_3$  and tear off a piece of the paper with the

adhering precipitate. Roll this into a small mass, place it in a crucible and moisten with not more than 5 drops of 0.3*n*  $\text{Co}(\text{NO}_3)_2$  solution. Heat until the paper is charred. Withdraw the flame occasionally to determine when the blue color develops. See Plate III, *E*.

5. There is no characteristic bead test.

6. What is the possibility of displacing  $\text{Al}^\circ$  from its salts in solution by other metals?

### EXERCISES

1. In the hydrolysis of aluminum acetate, why must the acidity be low? Is a solution of aluminum chloride acid?

2. Compare the color and solubilities of the basic acetates of iron and aluminum.

3. What radicals can be identified by Thénard's blue?

4. Traces of aluminum compounds are often found in the course of analysis. What may be their sources?

5. Explain, with the necessary reactions, why  $\text{Al}(\text{OH})_3$  and not  $\text{Al}_2(\text{CO}_3)_3$  is precipitated when a soluble carbonate is added to a solution of an aluminum salt.

6. Will a large excess of ammonium salts prevent the precipitation of  $\text{Al}(\text{OH})_3$  in Exercise 5? (There are several points to be considered in this answer.)

### CHROMIUM-ION, $\text{Cr}^{+3}$ (VIOLET OR GREEN)

Chromium exhibits three plus valences: +2 in chromous compounds; +3 in chromic compounds and chromites; and +6 in chromates and dichromates. The transition from metallic to non-metallic radical occurs in the dual ionization of chromic hydroxide. There is no unit change in valence in going from a chromate to a dichromate. Would perchromate be a correct name for a dichromate?

The chromous compounds, like the ferrous, are readily oxidized in solution to chromic. Oxygen from the air or dissolved in water can bring about the change.

Our preliminary tests will begin with  $\text{Cr}^{+3}$  and not with  $\text{Cr}^{++}$ , because that is the lowest valence that chromium has in Group III. Even where a chromate has been present in Group II the  $\text{H}_2\text{S}$  reduction stops at  $\text{Cr}^{+3}$ .

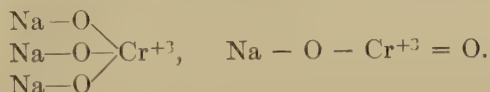
1. **Chromic Hydroxide,  $\text{Cr}(\text{OH})_3$ .**—Precipitate  $\text{Cr}(\text{OH})_3$  by adding  $\text{NH}_4\text{OH}$  in slight excess to a test solution of  $\text{Cr}(\text{NO}_3)_3$ . Describe the precipitate. See Plate II, *L*. Take a part of this



precipitate in a test tube and add 5 cc. concentrated  $\text{NH}_4\text{OH}$ . A slightly violet-colored solution will indicate a partial solution of the precipitate by forming ammonia complexes. Carefully boil to expel the excess ammonia and note the attendant fading of the violet color. What are the best conditions for the precipitation of  $\text{Cr}(\text{OH})_3$  by  $\text{NH}_4\text{OH}$ ? Will the precipitate dissolve in  $2n$   $\text{HCl}$ ?

Take a test solution of  $\text{Cr}(\text{NO}_3)_3$  and precipitate with  $\text{KOH}$  or  $\text{NaOH}$  in slight excess. Is the precipitate the same as that obtained with  $\text{NH}_4\text{OH}$ ? Add the reagent in sufficient excess to dissolve all of the precipitate. Conclusion? Reprecipitate by adding  $\text{HCl}$  until solution is almost neutral. Completely dissolve a part of the  $\text{Cr}(\text{OH})_3$  in excess  $\text{HCl}$ . Write the two equations for the two methods of putting the precipitate into solution. Will it dissolve in acetic acid?

Sodium chromite, the salt resulting from the solution of  $\text{Cr}(\text{OH})_3$  in excess  $\text{NaOH}$ , is usually written  $\text{Na}_3\text{CrO}_3$ , but undoubtedly consists in a large measure of  $\text{NaCrO}_2$ . The valence of chromium is the same in each, as the structural formulas show:



In what way do the two formulas for chromous acid differ? What is the color of a chromite solution? Determine the effect of boiling the solution. If you were to have a mixed precipitate of  $\text{Al}(\text{OH})_3$  and  $\text{Cr}(\text{OH})_3$ , and this is first dissolved in an excess  $\text{NaOH}$  and then boiled, what would be the result?

Add a solution of  $(\text{NH}_4)_2\text{S}$  to a test solution of  $\text{Cr}(\text{NO}_3)_3$ . What is the precipitate? How does it compare with those already obtained in this section? The reaction is analogous to that involving salts of aluminum. Write the equation.

To promote hydrolysis we usually add water and boil. Is there any objection to this procedure with salts of chromium?

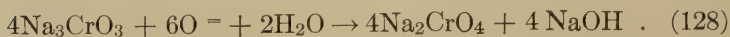
What will be precipitated when  $\text{Na}_2\text{CO}_3$  is used as the reagent? Show the reaction by equations.

**2. Sodium Chromate,  $\text{Na}_2\text{CrO}_4$ .**—A chromate may result from the oxidation of a chromite and forms simultaneously with the solution of chromic hydroxide by a strong base where an oxidizing agent is present.

Take one of the sodium chromite solutions obtained in the last

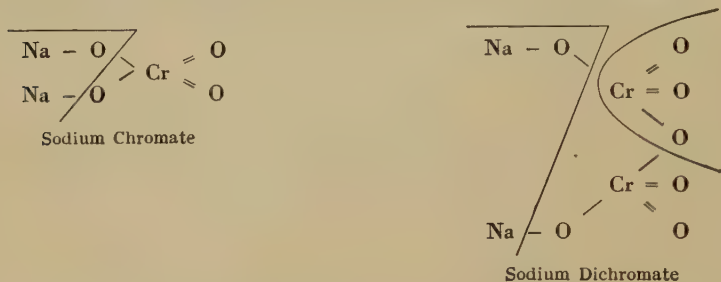


section and slowly add a little  $\text{Na}_2\text{O}_2$  powder. Make the addition cautiously by dropping in only a few granules at a time. Warm between additions and stop when the solution has changed from green to yellow. The reactions are:

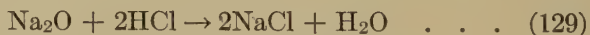


Refer to the section on oxidizing agents for a review of the electron change in oxidations by  $\text{Na}_2\text{O}_2$ .

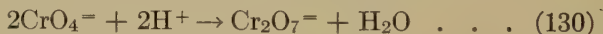
**3. Sodium Dichromate,  $\text{Na}_2\text{Cr}_2\text{O}_7$ .**—We shall compare first the structural formulas of sodium chromate and dichromate:



The chromate is essentially  $\text{Na}_2\text{O} \cdot \text{CrO}_3$ , and the dichromate,  $\text{Na}_2\text{O} \cdot 2\text{CrO}_3$ . In changing from two molecules of a chromate to one of a dichromate,  $\text{Na}_2\text{O}$  is removed. This is done by  $2\text{H}^+$  from an acid as:

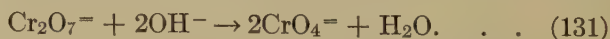


Another method of representing the reaction is:



Is the reverse reaction hydrolysis? Give a reason for your answer.

In changing one molecule of dichromate into two molecules of chromate we are essentially adding  $\text{Na}_2\text{O}$ . This is accomplished by the addition of  $2\text{NaOH}$ , and  $\text{H}_2\text{O}$  is eliminated as shown by:



Add  $\text{HCl}$ , dropwise, to a solution of potassium chromate until the color has changed from yellow to orange-red. Now reverse the color change by adding  $\text{NaOH}$ .

The reduction of dichromates to chromates and chromic salts by  $\text{H}_2\text{S}$  can be shown by taking a dilute solution of  $\text{Na}_2\text{Cr}_2\text{O}_7$  and slowly passing  $\text{H}_2\text{S}$  through the solution. The color should change from orange-red to yellow and finally to green when  $\text{Cr}^{+3}$  is predominating. A precipitate may also separate. Of what does it consist? Write equations to show the steps involved in the reduction. What will be the effect of adding  $\text{HCl}$  before reducing with  $\text{H}_2\text{S}$ ?

**4. Perchromic Acid,  $\text{H}_7\text{CrO}_{10}$ .**—The non-metallic radicals containing chromium belong more specifically to the cation group but they must also be considered in a limited way in a study of the anions. The identification of  $\text{CrO}_4^{=}$ , for example, is also an identification of  $\text{Cr}$ .

Take 2 cc.  $\text{Na}_2\text{CrO}_4$  solution, make acid with  $\text{HNO}_3$  and pour into a test tube containing 3 cc. ether and 2 cc. concentrated  $\text{H}_2\text{O}_2$  solution. Mix carefully and permit to settle. The blue molecules of  $\text{H}_7\text{CrO}_{10}$  will be concentrated in the ether layer (see Plate V, *I* and *J*). In *I* the color has not been concentrated by an ether layer. Why is the color more prominent in the ether layer?

**5. Chromic Basic Acetate,  $\text{Cr}(\text{OH})_2\text{Ac}$ .**—Add sodium acetate solution to a test solution of  $\text{Cr}(\text{NO}_3)_3$ . If no precipitate results, try boiling and the addition of water as you did in similar tests with  $\text{Fe}^{+3}$  and  $\text{Al}^{+3}$ . No precipitate should result. If solutions of iron and aluminum are added, the basic acetates of all three will be precipitated. Can you explain this? (Don't be discouraged if you can't.)

**6. Additional Precipitate of Chromic-ion.**—Chromic phosphate,  $\text{CrPO}_4$ , green.

**7. Borax bead tests** in the oxidizing flame are shown in Plate VI, *L* and *R*. The color is a pale blue-green and is practically the same in the reducing flame.

### EXERCISES

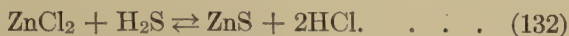
1. Which is the better oxidizing agent, a chromate or a dichromate? Answer this question from more than one viewpoint if possible.
2. Will the oxidizing value be affected by the  $[\text{H}^+]$  of the solution?
3. How would you test for the presence of  $\text{CrO}_4^{=}$ ? (Refer also to lead tests.)
4. Show, by comparing certain compounds of manganese and chromium, how an amphoteric substance can have the same change in metallic properties as a non-ampholyte, by a change in valence.



Research Laboratories of The Goodyear Tire and Rubber Company,  
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ZINC-ION,  $\text{Zn}^{++}$  (COLORLESS)

**1. Zinc Sulfide,  $\text{ZnS}$ .**—Pass  $\text{H}_2\text{S}$  through a test solution of  $\text{ZnCl}_2$  which is nearly neutral. Describe the precipitate:

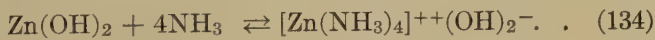


Repeat the experiment, but before passing  $\text{H}_2\text{S}$  through add some  $\text{HCl}$ . Is the amount of precipitate decreased? Again repeat the experiment by starting with two test tubes containing test solutions of  $\text{ZnCl}_2$ . To the first add acetic acid, and to the second add the same amount of acetic acid and some ammonium acetate. Pass  $\text{H}_2\text{S}$  through the two solutions. In which is the precipitate greater?

Filter some  $\text{ZnS}$  and test its solubility in  $2n$   $\text{HCl}$ ,  $6n$  acetic acid,  $\text{NaOH}$  and  $\text{NH}_4\text{OH}$ .

Take 5 cc. test solution of  $\text{ZnCl}_2$ , make slightly alkaline with  $\text{NH}_4\text{OH}$  and pass  $\text{H}_2\text{S}$  through. Filter. Has any  $\text{ZnS}$  passed into the filtrate? Add some  $\text{NH}_4\text{Cl}$  and boil. What are the best conditions for precipitation? Wash the precipitate with water containing a little  $\text{NH}_4\text{Cl}$ . What is the purpose of the  $\text{NH}_4\text{Cl}$ ? If you are unable to decide, wash another portion of  $\text{ZnS}$  with water only, and then examine the filtrate.

**2. Zinc Hydroxide,  $\text{Zn}(\text{OH})_2$ .**—Add  $\text{NH}_4\text{OH}$  to a test solution of  $\text{ZnCl}_2$  until precipitation is just complete. Now add an excess. Solution is caused by the formation of an ammonia complex.

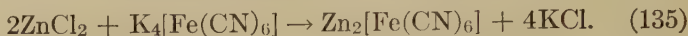


Will the presence of ammonium salts assist or retard this solution? First determine the fact experimentally and later, as an exercise, try to explain from theoretical considerations.

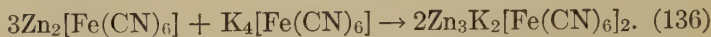
Precipitate  $\text{Zn}(\text{OH})_2$  by adding  $\text{NaOH}$  in slight excess to a test solution of  $\text{ZnCl}_2$ . Now add a large excess until complete solution results. Write the equation. What is the name of this salt formed? Try the effect of boiling the solution. Add more  $\text{NaOH}$  if  $\text{Zn}(\text{OH})_2$  precipitates upon boiling.



**Zinc Potassium Ferrocyanide,  $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$ .**—Add a few drops of potassium ferrocyanide to a test solution of zinc chloride. The white precipitate is formed as follows:



The precipitate changes when an excess of reagent is added as shown by:



**4. Rinmann's Green,  $\text{CoO}$ ,  $\text{ZnO}$ .**—Prepare in a manner similar to that for Thénard's blue in the aluminum section. See Plate III, *F*.

### EXERCISES

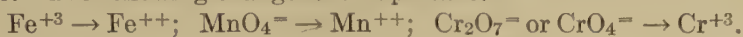
1. Show the equilibria by which  $\text{NH}_4\text{OH}$  supplies  $\text{NH}_3$ .
2. By considering the equilibria involved, show the effect of  $\text{NH}_4\text{Cl}$  upon the solubility of  $\text{ZnS}$  in  $\text{NH}_4\text{OH}$ .
3. Give several methods for precipitating  $\text{Zn}(\text{OH})_2$  from a solution of  $\text{Na}_2\text{ZnO}_2$ .
4. What will be the effect of adding  $\text{Na}_2\text{O}_2$  to a test solution of  $\text{ZnCl}_2$ ?
5. Suggest methods for detecting  $\text{Al}^{+3}$ ,  $\text{Cr}^{+3}$  and  $\text{Zn}^{++}$  when in the same solution.
6. Make a list of the hydroxides of the radicals in Group III and give the solubilities in  $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{HCl}$  and  $\text{HAc}$ .
7. Make a similar list for the sulfides.
8. Which of the hydroxides and sulfides can be precipitated in the presence of ammonium salts?
9. Explain why each of the following solutions has a decreasing value of  $[\text{H}^+]$ : (a)  $\text{HCl}$ , (b)  $\text{HAc}$ , (c)  $\text{HAc}$  to which has been added  $\text{NH}_4\text{Ac}$ .
10. Will  $\text{ZnS}$  be precipitated most completely from (a) an ammoniacal solution to which is added  $(\text{NH}_4)_2\text{S}$ , (b) a solution which is acid by  $\text{HAc}$ , or (c) a solution acid by  $\text{HAc}$  and containing  $\text{NH}_4\text{Ac}$ ? Discuss from as many viewpoints as possible and write the necessary equations.

### SUMMARY OF REACTIONS OF THE IONS IN GROUP III THAT ARE OF IMPORTANCE IN ANALYTICAL PROCEDURE

It has been determined in the preliminary tests that the radicals of Group III cannot be precipitated in Group II. The solubility products of the sulfides of Group III cannot be exceeded by the concentrations of the metal radicals used and the maximum concentration of the sulfide radical from  $\text{H}_2\text{S}$  which it is possible to have present in  $0.3n$   $\text{HCl}$ .



Where Group III results as the filtrate from Group II, the valence of its radicals is partly determined by the reducing action of  $\text{H}_2\text{S}$ . The following changes are important:



In the precipitation of Group III the solubilities of the hydroxides and sulfides as well as the solubility of  $\text{Mg}(\text{OH})_2$ , which is usually included in a succeeding group, must be carefully reviewed.

If all of the radicals are to be precipitated at the same time, there is but one procedure to follow, that is, to add  $(\text{NH}_4)_2\text{S}$  to an ammoniacal solution.  $\text{NH}_4\text{OH}$  cannot be used alone because the hydroxides of  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Zn}^{++}$  and to a small extent  $\text{Mn}^{++}$  would go into solution as ammonia complexes. This would leave  $\text{Fe}^{+3}$ ,  $\text{Cr}^{+3}$ ,  $\text{Al}^{+3}$  and possibly  $\text{Mn}^{+3}$  in the precipitate.

The hydroxide of magnesium must also be taken into account at this time because its  $K_{\text{sp}}$  is  $3.2 \times 10^{-11}$  and can be exceeded in a solution containing much of an excess of  $\text{NH}_4\text{OH}$ . The solubilities of  $\text{Mg}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$  are  $2 \times 10^{-4}$  and  $1.3 \times 10^{-4}$ , respectively. This shows how closely  $\text{Mg}^{++}$  would come to precipitating with  $\text{Zn}^{++}$  in Group III if  $\text{NH}_4\text{OH}$  alone were considered as the precipitating agent. Since, however, the hydroxide of magnesium is more soluble than the hydroxides of the radicals studied in the preliminary tests for Group III, it would still be possible to eliminate  $\text{Mg}(\text{OH})_2$  from the group by reducing the  $[\text{OH}^-]$  to the extent that its  $K_{\text{sp}}$  would not be exceeded but that there would be saturation values obtained for members of Group III. This can be accomplished by the addition of ammonium salts. If, however, ammonium salts are used, one point must be noticed:  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Mn}^{++}$ , and  $\text{Zn}^{++}$  will not be completely precipitated in the group because their hydroxides are soluble in an excess of  $\text{NH}_4\text{OH}$  and ammonium salts. In other words, the hydroxide group, with  $\text{NH}_4\text{OH}$  as the group reagent and with ammonium salts present to keep  $\text{Mg}(\text{OH})_2$  in solution, reduces to  $\text{Fe}^{+3}$ ,  $\text{Cr}^{+3}$  and  $\text{Al}^{+3}$  with possibly some  $\text{Mn}^{++}$  and  $\text{Zn}^{++}$  also present. The precipitation of  $\text{Mn}(\text{OH})_2$  would also be uncertain because the question of exceeding its  $K_{\text{sp}}$  would depend upon the amount of ammonium salts added. Moreover, in the case of zinc, it has been found that the formation of the ammonia complex is not as complete as with those of cobalt and nickel.

A procedure followed by many is to precipitate Group III in two subdivisions, A and B. A is precipitated with  $\text{NH}_4\text{OH}$  in the

presence of a carefully regulated amount of ammonium salt; *B*, which is the filtrate of *A*, is precipitated with  $(\text{NH}_4)_2\text{S}$ . Subdivision *A* would then consist of  $\text{Fe}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$ , and subdivision *B* would contain  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{MnS}$  and  $\text{ZnS}$ . In this grouping one of the preliminary tests with ferrous hydroxide must be considered. We have found that  $\text{Fe}(\text{OH})_2$  is somewhat soluble in  $\text{NH}_4\text{Cl}$ , that is, it would be incompletely precipitated in subdivision *A*. By boiling the filtrate from Group II, after adding a few drops of  $\text{HNO}_3$ , the iron is changed to  $\text{Fe}^{+3}$  and the difficulty is removed.

For the precipitation of all of the radicals of the group at one time, the reagent  $(\text{NH}_4)_2\text{S}$  in the presence of ammonium salts will give  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{MnS}$ ,  $\text{FeS}$ ,  $\text{Fe}_2\text{S}_3$ ,  $\text{ZnS}$ ,  $\text{Al}(\text{OH})_3$  and  $\text{Cr}(\text{OH})_3$ . The two hydroxides result only to a very limited extent from the hydrolysis of the corresponding sulfides. Since this method of precipitation is most generally followed we shall continue a summary of the tests on this basis.

Where  $2n$   $\text{HCl}$  is added to the mixed sulfides and hydroxides of the group and the time is limited to a few minutes, all will go into solution except  $\text{CoS}$  and  $\text{NiS}$ . A test for  $\text{Ni}^{++}$  can be made with dimethyl glyoxime in the ammoniacal solution just previous to the precipitation of the entire group with  $(\text{NH}_4)_2\text{S}$ . The bead test for cobalt is very satisfactory even in the presence of much nickel. The bead test for nickel, however, is obscured if cobalt is present. Where the preliminary dimethyl glyoxime test for  $\text{Ni}^{++}$  and the bead test for  $\text{Co}^{++}$  are not considered satisfactory, the precipitate of  $\text{CoS}$  and  $\text{NiS}$  can be dissolved in aqua regia and confirmatory tests made from this.

The filtrate containing the soluble chlorides of  $\text{Mn}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Fe}^{+3}$ ,  $\text{Al}^{+3}$ ,  $\text{Cr}^{+3}$  and  $\text{Zn}^{++}$  can be precipitated with concentrated  $\text{NaOH}$ . This reagent, when added in large excess together with  $\text{Na}_2\text{O}_2$ , will separate the soluble aluminate, chromate and zincate from the insoluble hydroxides of manganese and iron.  $\text{Mn}^{+3}$  can be identified by the sodium carbonate fusion or by the red-violet color of the permanganate radical where a strong oxidizing agent is used.  $\text{Fe}^{+3}$  can be determined by dissolving some of the hydroxide precipitate in  $6n$   $\text{HCl}$  and making the ferrocyanide or the more delicate thiocyanate tests.

By neutralizing the strongly alkaline solution containing  $\text{AlO}_3^{-3}$  (or  $\text{AlO}_2^-$ ),  $\text{CrO}_4^-$  and  $\text{ZnO}_2^-$  with  $6n$   $\text{HCl}$ , then adding

$\text{NH}_4\text{Cl}$  and making slightly ammoniacal with  $\text{NH}_4\text{OH}$ , a precipitate of  $\text{Al}(\text{OH})_3$  will appear and can be separated and confirmed.

The filtrate now containing chromium and zinc after the aluminum has been removed can be subdivided and confirmatory tests made for the two radicals in separate portions.

All of the preliminary tests have been made in the absence of phosphates and organic matter. When these are present and the solution is made alkaline, precipitates may result which require special treatment. This situation is discussed in Part IV.

PROCEDURE FOR THE ANALYSIS OF A PRACTICE SOLUTION CONTAINING GROUP III IN THE ABSENCE OF SPECIAL INTERFERING IONS, AS PHOSPHATES, OXALATES AND ORGANIC MATTER IN GENERAL

When the solution has resulted as the filtrate from Group II it is assumed that it has been concentrated to 30 cc. by boiling, cooled and filtered until clear. If you are using a 25 cc. portion containing this group only, it should be of a concentration which will allow one-half of it to be taken for analysis. In this case dilute the half of the sample to 30 cc. with water.

**Precipitation of the Group.**—Add to either source of the group 10 cc.  $3n$   $\text{NH}_4\text{Cl}$ ,<sup>a</sup> and make alkaline with  $\text{NH}_4\text{OH}$ .<sup>b</sup> In a 3 cc. side test add dimethyl glyoxime for  $\text{Ni}^{++}$  and concentrate with ether. Discard the material used in the side test.<sup>a</sup> Heat the main solution in a flask nearly to boiling and add slowly<sup>c</sup> with constant stirring the reagent  $(\text{NH}_4)_2\text{S}^f$  in excess. Pass  $\text{H}_2\text{S}$  through for about two minutes. Bring to a boil<sup>o</sup> and at the end of two minutes test the vapor coming out of the flask with  $\text{PbAc}_2^h$  paper to insure an excess of reagent. Filter immediately<sup>i</sup> with suction and wash first with water containing a little  $(\text{NH}_4)_2\text{S}$  and finally once with distilled water. Where there are subsequent groups present, the filtrate should be acidified with  $\text{HAc}$ ,<sup>j</sup> concentrated to 20 cc., filtered and set aside in a stoppered test tube.

**Separation of the Group Precipitate into Two Subdivisions.**—Transfer the precipitate by means of a spatula to an evaporating dish and add 20 cc.  $2n$   $\text{HCl}$ .<sup>k</sup> Stir thoroughly with a glass rod for ten minutes but do not warm.<sup>l</sup> Filter and wash once with water. The residue, sub-division A, contains  $\text{CoS}$ ,  $\text{NiS}$  and  $\text{S}$ . In the filtrate subdivision B, are the soluble chlorides,  $\text{MnCl}_2$ ,  $\text{FeCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{AlCl}_3$  and  $\text{CrCl}_3$ .

**Analysis of Subdivision A. Separation and Identification of Cobalt and Nickel.**—Make a borax bead test for cobalt and nickel. A **blue bead** indicates cobalt; a **brown bead**, nickel. Besides the preliminary test for nickel and the bead test for cobalt and nickel, an additional test can be made by transferring the residue of  $\text{CoS}$ ,  $\text{NiS}$  and  $\text{S}$  to an evaporating dish where it is digested with aqua regia for ten minutes. After it has been evaporated nearly to dryness,<sup>m</sup> 5 cc.  $n$   $\text{HCl}$  are added and it is filtered and washed once with water. Then  $\text{NaOH}$  is added until alkaline. The green precipitate of  $\text{Ni}(\text{OH})_2$  should be noticeable in the mixed hydroxides of cobalt and nickel. Dissolve in  $\text{HAc}$  in slight excess<sup>n</sup> and divide the solution into two parts. Make the first alkaline with  $\text{NH}_4\text{OH}$  and repeat the dimethyl glyoxime test for nickel. If there were any conflicting circumstances present when the preliminary test was made they have now been removed. For the cobalt confirmatory test, use the other part of the solution and precipitate either with potassium nitrite or  $\alpha$ -nitroso- $\beta$ -naphthol.<sup>o</sup> The yellow precipitate of potassium cobaltinitrite  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ , or the red precipitate of cobalti-nitroso- $\beta$ -naphthol  $\text{Co}[\text{C}_{10}\text{H}_6(\text{NO})\text{O}]_3$  confirms cobalt.

**Analysis of Subdivision B. Separation of Manganese and Iron from Aluminum, Chromium and Zinc.**—Boil the filtrate containing the soluble chlorides of  $\text{Mn}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Fe}^{+3}$ ,  $\text{Al}^{+3}$ ,  $\text{Cr}^{+3}$  and  $\text{Zn}^{++}$  until there is no further test for  $\text{H}_2\text{S}$  in the escaping steam<sup>p</sup>. Filter if not perfectly clear and neutralize with strong  $\text{NaOH}$ . Now add 2 cc. in excess and 1 gram of  $\text{Na}_2\text{O}_2$ <sup>q</sup> in small portions and with constant stirring with a glass rod. Boil for about three minutes, dilute with 15–20 cc. water, filter and wash once with hot water. The precipitate consists of  $\text{Mn}(\text{OH})_3$  (and  $\text{MnO}(\text{OH})_2$ ) and  $\text{Fe}(\text{OH})_3$ . In the filtrate are  $\text{Na}_3\text{AlO}_3$  (or  $\text{NaAlO}_2$ ),  $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{ZnO}_2$ .

**Separation and Identification of Manganese and Iron.**—Take the brown precipitate of the hydroxides of iron and manganese and use a small portion for the sodium carbonate fusion test for  $\text{Mn}$ .<sup>r</sup> The green  $\text{Na}_2\text{MnO}_4$  in the fused mass indicates manganese. Another small part can be dissolved in concentrated  $\text{HNO}_3$  and boiled with  $\text{PbO}_2$  for the characteristic pink  $\text{MnO}_4^-$  ion.

Iron can now be tested for by dissolving some of the mixed hydroxides in a few drops of  $6n$   $\text{HCl}$ <sup>s</sup>, diluting with water and adding to a part of the solution of  $\text{FeCl}_3$  a few drops of  $\text{K}_4[\text{Fe}(\text{CN})_6]$



giving the blue precipitate of  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ . To another part may be added a few drops of  $\text{NH}_4\text{SCN}$  or  $\text{KSCN}$  which gives the characteristic red color of molecular  $\text{Fe}(\text{SCN})_3$ .

**Separation and Identification of Aluminum.**—Neutralize the strongly alkaline solution containing  $\text{Na}_3\text{AlO}_3$  (or  $\text{NaAlO}_2$ ),  $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{ZnO}_2$  with concentrated  $\text{HNO}_3$ . Add 5 cc.  $3n$   $\text{NH}_4\text{Cl}$  and make alkaline with  $\text{NH}_4\text{OH}$  in slight excess. Bring to a boil and note the gelatinous precipitate of  $\text{Al}(\text{OH})_3$ . Confirm with the aluminon reagent which gives a red suspension or by fusing with a few drops of  $0.3n$  cobalt nitrate solution which results in the blue compound,  $\text{Co}(\text{AlO}_2)_2$ .

**Separation and Identification of Chromium.**—After  $\text{Al}(\text{OH})_3$  has been removed, the filtrate contains  $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{ZnO}_2$  (and  $\text{Zn}(\text{NH}_3)_4^{++}$ ).<sup>4</sup> Acidify with  $\text{HAc}$ , add 4 cc.  $3n$   $\text{NH}_4\text{Ac}$ . Warm and precipitate by adding, dropwise,  $\text{BaCl}_2$  solution in excess. Bring to a boil in order to consolidate the precipitate, filter and wash once with hot water. The precipitate is  $\text{BaCrO}_4$ ,<sup>u</sup> and identifies chromium and the filtrate contains a solution of zinc salts. The precipitate of  $\text{BaCrO}_4$  can be confirmed by dissolving in  $6n$   $\text{HNO}_3$  and pouring the  $\text{Cr}(\text{NO}_3)_3$  solution into a test tube containing 3 cc. ether and 2 cc. strong  $\text{H}_2\text{O}_2$ . The blue color of molecular  $\text{H}_7\text{CrO}_{10}$  in the ether layer again confirms chromium. Where this test fails, the  $\text{H}_2\text{O}_2$  has decomposed.

**Final Precipitation of Zinc.**—Precipitate  $\text{ZnS}$  from the solution containing the zinc salts by passing  $\text{H}_2\text{S}$  through the solution in slight excess. If the precipitate is much discolored, filter, transfer to an evaporating dish, and digest with  $6n$   $\text{NaOH}$ . Dilute with an equal volume of water, make acid with conc.  $\text{HAc}$  and reprecipitate with  $\text{H}_2\text{S}$ . A further confirmation can be obtained by fusing the  $\text{ZnS}$  with a few drops of a  $0.3n$  solution of  $\text{Co}(\text{NO}_3)_2$  which results in the green substance  $\text{CoO} \cdot \text{ZnO}$ .<sup>o</sup>

#### NOTES ON THE PROCEDURE FOR THE ANALYSIS OF GROUP III

a. By the common-ion effect, the addition of  $\text{NH}_4\text{Cl}$  reduces the concentration of  $\text{OH}^-$  from the  $\text{NH}_4\text{OH}$  added later to such a small value that  $[\text{Mg}^{++}][\text{OH}^-]^2$  cannot exceed  $K_{\text{sp}}$  for that hydroxide.

b. Test with litmus. The solution must be alkaline and the slight formation of precipitates does not necessarily indicate alkalinity. You are going to precipitate the group partly as sulfides but, of course, hydroxides will appear at this point.

c. The presence of a precipitate does not interfere with the dimethyl



glyoxime test for nickel. The ether which is used in the test will concentrate the color. Always add the ether whether a pink color appears or not. The red molecules may be adsorbed by the precipitate present. They will be removed, however, by the ether.

d. Considerable care must be exercised in disposing of side-test material. It can often be added to the main solution, while in other cases it must be discarded.

e. Reagents are always to be added in small amounts. Here the NiS will be put in a colloidal state if the addition is not made slowly and to a hot solution.

f. It is supposed that the reagent is in suitable condition, that is, contains the necessary amount of  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{S}$ . Since both substances may decompose, it is necessary to pass a small amount of  $\text{H}_2\text{S}$  through the ammoniacal solution.

g. Boiling consolidates the precipitates as well as removes any large excess of reagent. This is especially desirable with NiS and  $\text{Cr}(\text{OH})_3$ .

h. The excess of precipitating reagent can always be tested for in the group filtrate, but in this case, since it decomposes into gases and boiling is necessary anyway, the test can be made before filtering. In making a test with  $\text{PbAc}_2$ , place a drop of the solution on a strip of filter-paper and hold in the escaping steam.

Cautions: (a) Do not moisten the strip in the lead acetate bottle. (b) Do not hold a dripping strip over the boiling solution. (c) Do not put the strip with the lead acetate into the solution which is being heated. Lead acetate in Group III will cause trouble. The PbS formed on the paper will frequently be yellow instead of black because of its state of dispersion. The PbS usually has a peculiar metallic glaze irrespective of its color.

i. The sulfides may be changed to soluble sulfates. In filtering here, it is advisable to keep the precipitate covered with liquid until the last. This will exclude the air.

j. The next group is precipitated as carbonates. If  $\text{SO}_4^{=}$  ions are formed in the filtrate the alkaline-earth group will be precipitated, in part at least, as sulfates. These are very insoluble and would not be changed by the carbonate reagent.

k. This volume of acid should be sufficient for the average group precipitate. Experience will enable you to judge the amount of solvent necessary to be used with various volumes of precipitates.

l. Warming will dissolve some of the CoS and NiS. Depend here upon stirring and not heating to promote solution.

m. Evaporating will remove the strong acids which would require an excessive amount of base to neutralize. The volumes of solution would be unnecessarily large.

n. The tests at this point require a solution either slightly acid with a weak acid or just alkaline. By precipitating and dissolving the washed precipitate in HAc, a solution that has a small  $[\text{H}^+]$  is obtained, and by adding  $\text{NH}_4\text{OH}$  the  $[\text{OH}^-]$  excess can likewise be kept low.

o. Refer to the preliminary tests for the details of these tests.

p. If  $\text{H}_2\text{S}$  is present when the filtrate is made alkaline, there will be a

partial precipitation as sulfides. The hydroxides and not the sulfides are desired.

q. It must be remembered that  $\text{Cr}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$  and  $\text{Zn}(\text{OH})_2$  are not only precipitated by the  $\text{NaOH}$  but are also redissolved by an excess. There must be a large excess of  $\text{NaOH}$  to insure complete precipitation and subsequent solution. Whenever  $\text{Na}_2\text{O}_2$  is used, a blank test must be made to see if it contains any iron. To do this add 1 gram  $\text{Na}_2\text{O}_2$  to water, heat to drive off excess gas, add concentrated  $\text{HCl}$  until acid and then add a few drops of  $\text{KSCN}$ . If a red color develops here, the depth of color must be considered in the procedure.

r. Refer to the preliminary tests for details of these confirmatory tests.

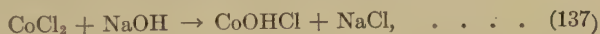
s. Under no conditions use  $\text{HNO}_3$ . When  $\text{KSCN}$  is added to a solution that is acid with  $\text{HNO}_3$ , a red solution will result also. Nitrates, however, should not be present at this point in the analysis.

t. The concentration of the ammonia complex will be a small quantity because the  $\text{NH}_4\text{OH}$  is only in slight excess.

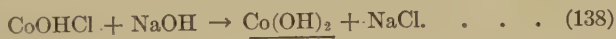
u. Remember that the concentration of  $[\text{H}^+]$  must be small in order to have  $\text{BaCrO}_4$  precipitate. This explains the use of  $\text{HAc}$  and  $\text{NaAc}$ .

v. The fusion tests that involve cobalt nitrate are of little value unless carefully done. It is frequently questioned whether the test gives any additional information.

Reference is again made to the precipitation of cobalt hydroxide which frequently gives trouble in analyses due to certain color changes. In a cold solution sodium hydroxide will precipitate a blue basic salt:



which changes into a pink cobaltous hydroxide, especially when the solution is warmed.



A difficulty is introduced on account of these color changes in precipitating  $\text{Mn}(\text{OH})_3$  from a solution of  $\text{MnCl}_2$  where there is a contamination of  $\text{CoCl}_2$ . The pink or red precipitate of  $\text{Co}(\text{OH})_2$  frequently darkens by exposure to the air and might lead one to infer that it was  $\text{Mn}(\text{OH})_3$ . The latter, however, is usually much darker and is essentially brown and not a dark red (see Plate II, *N*). The fusion test, if properly done, is not obscured by the presence of cobalt compounds.

### OPTIONAL TESTS IN THE ANALYSIS OF GROUP III

Instead of using  $(\text{NH}_4)_2\text{S}$  as a group reagent, the solution can be made alkaline with  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{S}$  passed through. When ammonium sulfide is properly made, however, and added in portions, no trouble should be experienced with colloidal  $\text{NiS}$ .

In separating cobalt from nickel the sulfides can be dissolved in aqua regia; then  $\text{KCN}$  added giving the complexes  $\text{K}_2[\text{Ni}(\text{CN})_4]$  and  $\text{K}_4[\text{Co}(\text{CN})_6]$ . It will be recalled that cobalt is the more readily oxidized or reduced. If a

solution of sodium hypobromite is now added to the solution of the complexes, nickel will be precipitated as black  $\text{Ni}(\text{OH})_2$  (or  $\text{Ni}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ).

A test for chromium is sometimes made in the solution of  $\text{Na}_2\text{CrO}_4$  by first making just acid with  $\text{HCl}$ , then 2 cc. of this solution are poured into a test tube containing 3 cc. dilute  $\text{KI}$  solution and 3 cc.  $\text{CS}_2$ . Mix thoroughly and note any color in the  $\text{CS}_2$  layer. Discard after two minutes as slow oxidation of the  $\text{KI}$  in the acid solution will occur whether chromic acid is present or not. In this test the chromic acid liberates free iodine which is extracted by the  $\text{CS}_2$ . A blank test should be made at the same time so that a standard of color can be established.

The principal alternative method in procedure involves the grouping of the two subdivisions. In our procedure we placed in subdivision *A* the radicals  $\text{Ni}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Fe}^{++}$  and  $\text{Fe}^{+3}$ . In subdivision *B* were the remaining radicals  $\text{Al}^{+3}$ ,  $\text{Cr}^{+3}$  and  $\text{Zn}^{++}$ .

In another type of procedure  $\text{Fe}^{+3}$ ,  $\text{Cr}^{+3}$  and  $\text{Al}^{+3}$  are placed in *A*. With this arrangement there is the possibility of some  $\text{Mn}^{++}$  and  $\text{Zn}^{++}$  also precipitating in subdivision *A*, but the situation is readily taken care of. A brief outline of this method follows, but the details must be obtained from the first procedure and in the preliminary tests.

**Second Method for the Analysis of Group III.**—Add 3 drops concentrated  $\text{HNO}_3$  to the solution and boil for five minutes to insure iron being in the higher valence. Cool, filter if necessary, add 10 cc. 3*n*  $\text{NH}_4\text{Cl}$  and make just alkaline with  $\text{NH}_4\text{OH}$ . Make a side test for  $\text{Ni}^{++}$  with dimethyl glyoxime and ether and then completely precipitate the group by adding 2 cc. 6*n*  $\text{NH}_4\text{OH}$ . Filter by suction and wash once with hot water. Subdivision *A* now consists of  $\text{Fe}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$ . Transfer precipitate to an evaporating dish and add 5 cc.  $\text{NaOH}$  and 1 gram  $\text{Na}_2\text{O}_2$ . Digest for five minutes, dilute with 10 cc. water, bring to a boil, filter and wash. The residue contains  $\text{Fe}(\text{OH})_3$  with perhaps some  $\text{Mn}(\text{OH})_3$ . Make a sodium carbonate fusion with a small part of the residue for a manganese test. The presence of iron will not interfere in this fusion. Dissolve another part of the residue in concentrated  $\text{HCl}$ , dilute and make the  $\text{K}_4[\text{Fe}(\text{CN})_6]$  or the  $\text{KSCN}$  test for iron.

The strongly alkaline filtrate is now divided into two parts for the chromium and aluminum tests. To the first portion add  $\text{HCl}$  until just acid, then add some  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  to alkalinity. The precipitate of  $\text{Al}(\text{OH})_3$  can be confirmed by any of the methods which have been given. The second part can be tested for chromium by making acid with  $\text{HNO}_3$  and then proceeding with the perchromic acid test in ether.

Returning to the filtrate from subdivision *A*, we first concentrate to about 30 cc., add 3 cc. more  $\text{NH}_4\text{Cl}$  and then make alkaline with  $\text{NH}_4\text{OH}$ . Two cubic centimeters in excess can be added. Heat to near boiling and precipitate with  $(\text{NH}_4)_2\text{S}$ . The entire procedure for precipitation, filtering and washing is the same as in the first procedure.

The separation of  $\text{CoS}$  and  $\text{NiS}$  from  $\text{MnCl}_2$  and  $\text{ZnCl}_2$ , and the subsequent treatment of the cobalt and nickel residue is also a duplication of the first procedure. The filtrate containing  $\text{MnCl}_2$  and  $\text{ZnCl}_2$  is boiled to expel  $\text{H}_2\text{S}$ , and  $\text{NaOH}$  is added in excess with 1 gram  $\text{Na}_2\text{O}_2$ . Dilute, boil, filter

and wash. The precipitate of  $\text{Mn(OH)}_3$  is tested by any of the methods given. The filtrate containing  $\text{Na}_2\text{ZnO}_2$  is made acid with  $\text{HAc}$ , then  $\text{NaAc}$  is added and  $\text{ZnS}$  is precipitated as previously described.

If, in the course of this second procedure, zinc gives trouble by remaining in subdivision A, the hydroxide precipitate containing the subdivision and the zinc contamination can be dissolved in  $6n$   $\text{HCl}$  and then reprecipitated with  $\text{NH}_4\text{OH}$  in considerable excess. After filtering and washing, the filtrate is added to the first one so that the entire solution can be analyzed for subdivision B.

## PROCEDURE SHEET V

## ANALYSIS OF GROUP III

Final tests are underscored twice

Precipitation of the group and separation into subdivisions A and B, in the absence of phosphates and other conflicting radicals.

Solution contains  $\text{Ni}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Fe}^{+3}$ ,  $\text{Al}^{+3}$ ,  $\text{Cr}^{+3}$ ,  $\text{Zn}^{++}$ .

If the solution results as the filtrate from Group II, it is assumed that it has been concentrated by boiling to about 30 cc., cooled and filtered if necessary.

Where the sample contains Group III only, one-half is taken for analysis and diluted with water to 30 cc.

Place solution in flask, add 10 cc.  $3n$   $\text{NH}_4\text{Cl}$  and make alkaline with  $\text{NH}_4\text{OH}$ . Make a side test for  $\text{Ni}^{++}$  by taking 3 cc. of the solution and adding a few drops of dimethyl glyoxime reagent and 3 cc. of ether. A red color of dissolved molecules of nickel dimethyl glyoxime in the ether layer indicates the presence of nickel.

Heat the main solution nearly to boiling and precipitate the group with  $(\text{NH}_4)_2\text{S}$  in excess. Pass  $\text{H}_2\text{S}$  through the solution for two minutes to insure complete precipitation. Boil slowly for two minutes and test vapor with  $\text{PbAc}_2$  paper to make sure that an excess of reagent is present even after boiling.

Filter immediately and wash with water containing a few drops of  $(\text{NH}_4)_2\text{S}$ .

Precipitate:  $\text{NiS}$ ,  $\text{CoS}$ ,  $\text{MnS}$ ,  $\text{FeS}$ ,  $\text{Fe}_2\text{S}_3$ ,  $\text{ZnS}$ ,  $\text{Al(OH)}_3$ ,  $\text{Cr(OH)}_3$ . Transfer to evaporating dish and add 20 cc.  $2n$   $\text{HCl}$ . Stir and digest for ten minutes. Filter and wash with water.

Filtrate: If succeeding groups are present, acidify with  $\text{HAc}$ , concentrate to 20 cc., filter and set aside in a stoppered container.

Residue, Subdivision  
A:  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{S}$ .

Filtrate, Subdivision B:  $\text{MnCl}_2$ ,  
 $\text{FeCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{CrCl}_3$ .



PROCEDURE SHEET VI  
ANALYSIS OF SUBDIVISION A, GROUP III

Final tests are underscored twice

Subdivision A consists of the residue CoS, NiS and S.

Make a borax bead test with a small amount of the residue. A blue bead indicates cobalt, but gives no information about nickel. A brown bead shows the absence of cobalt and confirms the presence of nickel.

Transfer residue to an evaporating dish, digest in aqua regia for about 10 minutes, evaporate nearly to dryness, add 5 cc. *n* HCl and filter.

Residue: <u>S</u> . Dis- card.	Filtrate: $\text{CoCl}_2$ and $\text{NiCl}_2$ . Make alkaline with NaOH, filter and wash precipitate with water.
	<p>Precipitate: <u><math>\text{Co}(\text{OH})_2</math></u>, (possibly <u><math>\text{Co-OH-Cl}</math></u>) and <u><math>\text{Ni}(\text{OH})_2</math></u>. Dissolve precipitate in HAc in slight excess. Make one-half of solution just alkaline with <math>\text{NH}_4\text{OH}</math>, add a few drops of dimethyl glyoxime and 3 cc. ether. Mix and settle. Red color of ether layer again confirms the presence of <u>nickel-dimethyl glyoxime</u>, a test for nickel.</p> <p>To the second half of the solution add a few drops of HAc, saturate with solid KCl and add a concentrated solution of <math>\text{KNO}_2</math> in excess. A yellow precipitate of potassium cobalti-nitrite, <u><math>\text{K}_3[\text{Co}(\text{NO}_2)_6]</math></u>, which may form only upon standing and warming, confirms cobalt.</p> <p>If the nitroso-<math>\beta</math>-naphthol reagent has given satisfactory tests in the preliminary work, the second half of the solution can be made more strongly acid with a few drops of HCl, warmed slightly, and 1 cc. nitroso-<math>\beta</math>-naphthol reagent added. A red precipitate of cobalti-nitroso-<math>\beta</math>-naphthol, <u><math>\text{Co}[\text{C}_{10}\text{H}_6(\text{NO})\text{O}]_3</math></u>, is an additional confirmatory test for cobalt.</p>



PROCEDURE SHEET VII  
ANALYSIS OF SUBDIVISION B, GROUP III

Final tests are underscored twice

Subdivision B contains a solution of  $\text{MnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{AlCl}_3$  and  $\text{CrCl}_3$ . Boil solution until vapor gives no test for  $\text{H}_2\text{S}$  with  $\text{PbAc}_2$  paper. Filter if turbid. Neutralize with strong  $\text{NaOH}$  and add 2 cc. in excess. Add 1 gram  $\text{Na}_2\text{O}_2$  in small portions and with constant stirring. Boil solution for three minutes after active evolution of gas has ceased. Dilute with 15–20 cc. water, filter and wash once with water.

Precipitate:  $\text{Mn}(\text{OH})_2$ , (and possibly  $\text{MnO}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_2$ ). Make a  $\text{Na}_2\text{CO}_3$  fusion with a small portion of the precipitate. A green precipitate of  $\text{Na}_2\text{MnO}_4$  confirms manganese. An additional test can be made by heating another small portion with conc.  $\text{HNO}_3$  and  $\text{PbO}_2$ . The pink solution containing  $\text{MnO}_4^-$  ions again confirms manganese.

Dissolve some of the ppt. in a few drops of  $\text{HCl}$ , dilute with water and add to one-half of the solution a few drops of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution. A blue ppt. of  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_3$  indicates iron. To the other half add a few drops of  $\text{KSCN}$  solution. A deep red color of  $\text{Fe}(\text{SCN})_3$  molecules also confirms iron.

Filtrate:  $\text{Na}_2\text{AlO}_2$ , (or  $\text{NaAlO}_2$ ),  $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{ZnO}_2$ . Neutralize with conc.  $\text{HNO}_3$ . Add 5 cc. 3*N*  $\text{NH}_4\text{Cl}$ , make alkaline with  $\text{NH}_4\text{OH}$ , boil, filter and wash.

Precipitate:  $\text{Al}(\text{OH})_3$ . Confirm by adding special dye to a suspension of the ppt. Characteristic color (red if "aluminum" is used) confirms aluminum.

Precipitate: A ppt. of yellow  $\text{BaCrO}_4$  indicates chromium.

A confirmatory test can be made by dissolving with  $\text{HNO}_3$ , adding  $\text{H}_2\text{O}_2$  and ether. Blue ether layer containing perchromic acid confirms chromium.

Filtrate: Soluble zinc salts. Pass  $\text{H}_2\text{S}$  through solution. White ppt. of  $\text{ZnS}$  indicates zinc. Confirm by fusing with a few drops of  $\text{Co}(\text{NO}_3)_2$ . A green mass containing  $\text{CoO} \cdot \text{ZnO}$  confirms zinc.

## CHAPTER VI

### GROUP IV.—THE AMMONIUM CARBONATE OR ALKALINE-EARTH GROUP

BARIUM,	Ba:	at. wt. 137.37:	Ba <sup>++</sup>
STRONTIUM, Sr:	at. wt. 87.63:	Sr <sup>++</sup>	
CALCIUM,	Ca:	at. wt. 40.07:	Ca <sup>++</sup>

This group consists of cations that have not been precipitated in preceding groups and are precipitated as carbonates in an ammoniacal solution containing ammonium chloride.

The radicals in this group are all bivalent and are placed in Group II of the periodic classification. It is the only qualitative group that has this uniformity in the periodic classification. The solubilities of the compounds of barium, strontium and calcium are quite similar and often vary in amount only and not in type. This fact often makes absolute separations within the group a difficult procedure.

The solubility of strontium occupies very uniformly the middle position between calcium and barium. The solubilities do not always increase from barium to calcium as with the sulfates, but may be in the reverse order from calcium to barium as with the oxalates.

#### FLAME TESTS

A very interesting division of qualitative analysis that is used very generally in the identification of the members of the alkaline-earth group consists in the flame test. The simplest form of this test is made with a clean platinum wire which has been dipped in a solution of the element or touched to the dry solid and then held in a non-luminous gas flame. The more exacting tests are made with a spectroscope.

**Platinum Wire Flame Tests.**—The platinum wire for the flame test is usually about 3 cm. long and is sealed into the end of a piece

of glass rod. The end of the wire can be kept straight or bent into a small loop around a pencil point as was done in the borax bead tests (see Plate VI). The wire must be thoroughly cleaned by alternately heating in the hottest part of a non-luminous gas flame and dipping into concentrated hydrochloric acid. A clean wire will impart no color to the flame, not even the very persistent yellow of sodium. If a yellow flame does persist, it indicates a contaminated cleaning solution.

In making a flame test, the end of the wire is dipped into the solution or touched to the solid and is then slowly brought into the side of the flame at about the level of the inner green cone. (See Fig. 8.) Dilute solutions rarely ever give satisfactory results. A few drops of the solution should be evaporated nearly to dryness, allowed to cool and a drop of 12*n* HCl added. Never completely evaporate a solution to dryness because the substance may be lost by volatilization or decomposed and some of the products volatilized. Hydrochloric acid is used to moisten the solid because chlorides as a group are quite volatile when heated and will therefore give a good test in the flame.

When a flame test is too indistinct for satisfactory identification a more intense color can be obtained by dipping the wire repeatedly into the solution and then bringing near enough to the flame to evaporate the liquid but not to volatilize the solid. After a few evaporations on the wire it is then carefully brought in the flame and the test should be more pronounced.

Not more than 1 cm. of the end of the wire should be dipped into the liquid because it will be almost impossible to reclean. This is especially true if the end of the glass rod has also been wet with the solution. A convenient place to keep the test wire when not in use is in a test tube containing the hydrochloric acid that is used for cleaning purposes. If the test tube is stoppered with a rubber stopper coated with vaseline it will prevent the acid from evaporating.

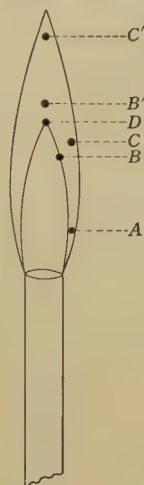


FIG. 8.—The Essential Divisions of a Gas Burner Flame.

A, region of relatively low temperature; B and B', reducing regions where there is high temperature and insufficient oxygen; C and C', oxidizing regions where there is high temperature and a good supply of oxygen; D, fusing zone or region of highest temperature. A flame test is usually made at the edge of the flame in the region of C.

Flame tests made with a platinum wire may not be entirely satisfactory. For example, in a fairly concentrated solution the crimson of strontium usually obscures for a few moments the flames of barium and calcium. In the absence of strontium the yellow flame of sodium will do the same thing. Fortunately the rate of volatilization of the compounds is not the same so that a small amount of the strontium compound may burn off and the green of barium or orange-red of calcium then become visible. When sodium is alone, the flame is an intense yellow but in the presence of calcium it becomes more or less an orange or reddish-yellow and it is impossible to decide whether calcium is present alone or whether both sodium and calcium are present in the substance.

Another source of error must be considered in the calcium flame test. In the complete analysis of the flame by means of the spectroscope there is a red line that is almost identical with that of strontium. It frequently happens that if a substance contains an excess of calcium this red wave length becomes very prominent and might be mistaken for the strontium flame.

The characteristic violet flame of potassium is so delicate that it is generally obscured when another flame is also present. A screen of blue glass can be used to cut off all but the potassium flame. Great care, however, must be exercised in its use. The so-called blue "cobalt" glass should never be used unless a preliminary test has been made with it. To do this, view a sodium flame through the glass and note whether a flame passes through. If it does it will appear blue and not yellow, so take two thicknesses of the glass or even a third piece if that is necessary to prevent approximately any wave lengths from coming through. When the potassium flame is now viewed through the combination it should be distinctly visible and the test will not be obscured by the presence of other flames. The combination of glasses that has proved satisfactory in the preliminary test should be used in all subsequent analyses.

A flame screen made of certain kinds of blue glass may give trouble by allowing a red line in the spectrum of potassium to be unduly prominent. This would lead one to believe that strontium was also present. This characteristic, however, should have been determined in the preliminary tests.

It is evident, therefore, that all of the flame tests with the excep-

tion, perhaps, of that of strontium should be considered more as preliminary tests and confirmed later in the course of the analysis.

**Spectroscopic Examination.**—Where a very exact analysis of a luminous flame is required, a spectroscope can be employed. The principle used in its construction is based upon the dispersion of light by a prism and is shown in Fig. 9.

When white light from any source passes through the slit *S* and then through the prism *P*, which is placed at the proper angle, the light will be dispersed or broken up into a series of wave lengths.

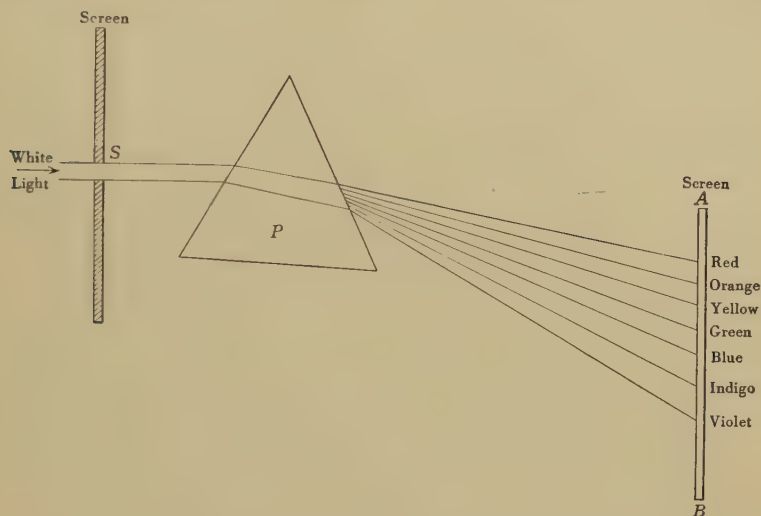


FIG. 9.—The Dispersion of White Light by a Prism.

*S*, slit in screen; *P*, prism; *AB*, white screen upon which the continuous spectrum falls.

A screen placed at *AB* will show the effect by a series of colors varying from violet to red. The series is in reality the blending of a multitude of images of the slit in different wave lengths and is known as a continuous spectrum. This type of spectrum is produced whenever a glowing or incandescent solid or liquid is used as the source of white light.

If the source of light does not furnish all of the wave lengths as with certain incandescent gases, then a discontinuous bright-line spectrum is formed and certain characteristic colored lines will be visible on the screen. Many elements can be identified by this type of spectrum because no two have the same combination.



There is a third type of spectrum, the absorption or dark-line spectrum, which we shall not consider.

The general arrangement of the spectroscope is shown in Fig. 10.

The source of light is placed at *A* in front of a slit in the collimator tube *B*. This tube passes parallel rays to the prism *C*. The dispersed rays from the prism then go through a viewing telescope *D* to the eye placed at *G*. In order to be able to locate the exact position of the various lines, a third tube *E* is introduced. At one end of this tube is placed a glass plate upon which is drawn a

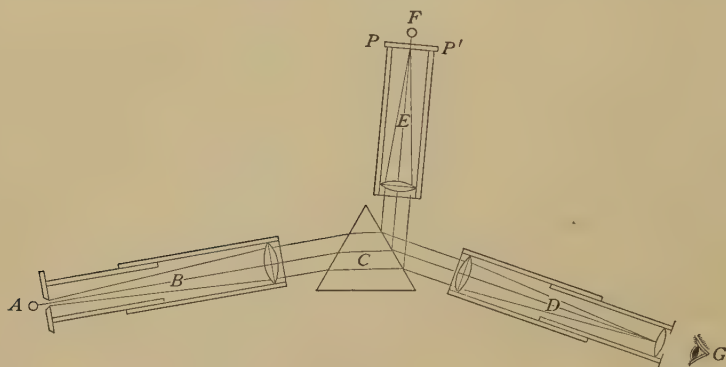


FIG. 10.—Analysis of a Luminous Gas Flame by Means of a Spectroscope.

*A*, position of flame to be analyzed; *B*, collimator; *C*, prism; *D*, viewing telescope; *P P'*, glass plate containing scale; *E*, tube used to project image of *P P'* upon prism; *F*, white light used to illuminate scale; *G*, position of eye in making examination.

fine scale. A light placed at *F* projects this scale upon one side of the prism and from there it is reflected to the eye at *G* in conjunction with the dispersed rays from *A*.

Although qualitative examination by means of a spectroscope is a very interesting development of the simple wire flame test and the dispersion of light by a prism, it must be remembered that it usually distinguishes very minute traces of an element. Since it is difficult to obtain solutions in a state of absolute purity it is evident that the use of the spectroscope in qualitative analysis must be carefully restricted.

## PRELIMINARY TESTS

BARIUM-ION,  $\text{Ba}^{++}$  (COLORLESS)

**1. Barium Carbonate,  $\text{BaCO}_3$ .**—Make 3 cc. test solution of  $\text{BaCl}_2$  distinctly alkaline with  $\text{NH}_4\text{OH}$ , then precipitate in a test tube with excess  $(\text{NH}_4)_2\text{CO}_3$ . Place the test tube in a beaker of hot water to settle the precipitate. Was there any turbidity developed during the addition of the  $\text{NH}_4\text{OH}$ ? Describe any changes that were noted during the settling of the carbonate precipitate.

The precipitation of the alkaline-earth group is not as satisfactory as with the preceding groups. In the first place, the carbonates are finely divided and unless consolidated by warming they will pass through the filter. The precipitate also forms very slowly at times so that it is difficult to know when an excess of reagent has been added. The  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  may be impure because of the absorption of  $\text{CO}_2$  from the air. What is the result if the  $\text{NH}_4\text{OH}$  contains some  $\text{CO}_2$ ? How will the  $(\text{NH}_4)_2\text{CO}_3$  be changed where there is an excess of  $\text{CO}_2$ ? How will the solubility of the carbonate change when there is an excess of  $\text{CO}_2$  in the reagent?

Filter the  $\text{BaCO}_3$  by decantation and wash once with cold water. Test its solubility in  $3n$   $\text{NH}_4\text{Cl}$ ,  $6n$   $\text{HAc}$  and  $n$   $\text{HCl}$ . Can  $\text{BaCO}_3$  be precipitated in a large excess of  $\text{NH}_4\text{Cl}$ ? Will it be necessary to have  $\text{NH}_4\text{Cl}$  present when this group is precipitated? Try to precipitate  $\text{BaCO}_3$  by diluting the same amounts of  $\text{BaCl}_2$  and  $(\text{NH}_4)_2\text{CO}_3$  that you first used with 25 cc. water and then mixing the solution together. What use are you going to make of these tests when you precipitate the group?

**2. Barium Hydroxide,  $\text{Ba}(\text{OH})_2$ .**—Try to precipitate  $\text{Ba}(\text{OH})_2$  by adding  $\text{NH}_4\text{OH}$  to 3 cc. test solution of  $\text{BaCl}_2$ . How could you determine whether a resulting precipitate is a hydroxide or a carbonate?

Dissolve the outside of a small piece of solid  $\text{NaOH}$  (do not handle with fingers or metal forceps) in water, wash once with distilled water, place in a clean test tube and add more distilled water. Add some of this solution to a test solution of  $\text{BaCl}_2$ . Describe the precipitate, and write the equation for the reaction. Test the solubility of the precipitate in hot water and in acetic acid.

**3. The Non-formation of Barium Sulfide,  $\text{BaS}$ , in an Aqueous Solution.**—Add some of the  $(\text{NH}_4)_2\text{S}$  reagent used in Group III to 5 cc. test solution of  $\text{BaCl}_2$ . Does the result give the reason for the absence of barium from Group III?

**4. Barium Sulfate,  $\text{BaSO}_4$ .**—Precipitate  $\text{BaSO}_4$  by adding  $n$   $\text{H}_2\text{SO}_4$  to 3 cc. test solution of  $\text{BaCl}_2$ . Settle by warming as you did with the carbonates. Repeat by replacing  $\text{H}_2\text{SO}_4$  with a saturated solution of  $\text{K}_2\text{SO}_4$ . Repeat again, and use  $(\text{NH}_4)_2\text{SO}_4$  as the precipitating reagent. What conclusion can you draw as to the solubility of  $\text{BaSO}_4$  in acid, neutral and alkaline solutions? Fuse on a porcelain crucible cover some of the  $\text{BaSO}_4$ , which has been washed by decantation, with one-half gram of solid  $\text{Na}_2\text{CO}_3$ . Heat strongly for ten minutes, cool, extract the fused mass with hot water in a beaker, using a glass rod to break up the mass. Filter and wash once with water. The precipitate is  $\text{BaCO}_3$  and some unconverted  $\text{BaSO}_4$ . The  $\text{BaCO}_3$  can now be easily put into solution by treating the precipitate with  $\text{HCl}$  or  $\text{HAc}$ .

**5. Barium Chromate,  $\text{BaCrO}_4$ .**—Add 1 cc.  $3n$   $\text{K}_2\text{CrO}_4$  to 3 cc. cold solution of  $\text{BaCl}_2$ . Describe the result. Repeat, but first dilute the  $\text{BaCl}_2$  solution with 20 cc. water, heat nearly to boiling and add the  $\text{K}_2\text{CrO}_4$  solution dropwise. Which method of precipitation gives the better results? If in doubt filter each precipitate and compare the filtrates. Test the solubility of  $\text{BaCrO}_4$  in acetic acid and in  $6n$   $\text{HCl}$ . Recall the  $\text{PbCrO}_4$  test in Group I.

**6. Barium Oxalate,  $\text{BaC}_2\text{O}_4$ .**—Add  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  to 3 cc. test solution of  $\text{BaCl}_2$ . Allow to settle but do not warm. Wash by decantation and test the solubility of the precipitate in boiling water and in  $6n$   $\text{HAc}$ . Warm the precipitate with the acid to determine if complete solution can be obtained. Would you use oxalic acid to precipitate  $\text{BaC}_2\text{O}_4$ ?

**7. Additional Precipitates of Barium-ion.**—Barium phosphate,  $\text{BaHPO}_4$  or  $\text{Ba}_3(\text{PO}_4)_2$ , white; barium sulfite,  $\text{BaSO}_3$ , white, practically insoluble in excess  $\text{H}_2\text{SO}_3$ ; barium potassium ferrocyanide,  $\text{BaK}_2[\text{Fe}(\text{CN})_6]$ , white.

**8. Flame Test.**—Make a flame test with a solution of  $\text{BaCl}_2$  and compare with Plate IV, A.

## EXERCISES

1. How could you prepare  $(\text{NH}_4)_2\text{CO}_3$  so that it would not contain an excess of  $\text{CO}_2$ ?
2. Calculate the approximate concentrations of  $[\text{Ba}^{++}]$  and  $[\text{OH}^-]$  present in a solution when you add 5 cc. 0.1*n*  $\text{NH}_4\text{OH}$  to 3 cc. test solution of  $\text{BaCl}_2$ . By comparing the ion-product with  $K_{\text{SP}}$  for  $\text{Ba}(\text{OH})_2$ , decide whether precipitation should take place.
3. Discuss the possibility of  $\text{BaS}$  forming in an ammoniacal sulfide solution. Refer to the section on aluminum-ion and then write the equations that are necessary to explain this reaction.
4. Explain how  $\text{BaSO}_4$ , by fusing with  $\text{Na}_2\text{CO}_3$ , is changed into  $\text{BaCO}_3$ .

STRONTIUM-ION,  $\text{Sr}^{++}$  (COLORLESS)

1. **Strontium Carbonate,  $\text{SrCO}_3$ .**—Precipitate  $\text{SrCO}_3$  from 3 cc. test solution of  $\text{Sr}(\text{NO}_3)_2$  by first making ammoniacal and then adding  $(\text{NH}_4)_2\text{CO}_3$  in excess. Settle by placing the test tube in warm water. Decant, wash once with water and test the solubility of the precipitate in 6*n*  $\text{HAc}$ , *n*  $\text{HCl}$  and strong  $\text{NH}_4\text{Cl}$ .

2. **Strontium Hydroxide,  $\text{Sr}(\text{OH})_2$ .**—Determine whether the hydroxide can be precipitated with  $\text{NH}_4\text{OH}$  and with  $\text{NaOH}$ .

3. **Strontium Sulfate,  $\text{SrSO}_4$ .**—Precipitate  $\text{SrSO}_4$  from an ammoniacal solution of  $\text{Sr}(\text{NO}_3)_2$  by adding  $(\text{NH}_4)_2\text{SO}_4$  in excess. Warm and permit to settle. Decant and wash once with water. Test the solubility of the precipitate in 6*n*  $\text{HAc}$ , *n*  $\text{HCl}$  and strong  $\text{NH}_4\text{Cl}$ . Test the solubility in hot water by boiling, filtering, concentrating to 2 cc., cooling, making ammoniacal and adding a few drops of  $(\text{NH}_4)_2\text{SO}_4$ .

Take 2 cc. each of test solutions of  $\text{BaCl}_2$  and  $\text{Sr}(\text{NO}_3)_2$  and add to each, alternately and dropwise, a saturated solution of  $\text{CaSO}_4$ . The test solutions must be of equal molarity and the  $\text{CaSO}_4$  must be saturated. Does the sulfate of barium or that of strontium precipitate first? Does this experiment fix the solubility of  $\text{CaSO}_4$  with respect to  $\text{BaSO}_4$  and  $\text{SrSO}_4$ ?

4. **Strontium Chromate,  $\text{SrCrO}_4$ .**—Take two test tubes with 3 cc. test solution of  $\text{Sr}(\text{NO}_3)_2$  in each. Add to one 3 cc. 6*n*  $\text{HAc}$ . Now add 2 cc.  $\text{K}_2\text{CrO}_4$  to each tube. Give results and compare with  $\text{BaCrO}_4$ .

5. **Strontium Oxalate,  $\text{SrC}_2\text{O}_4$ .**—Obtain a precipitate of  $\text{SrC}_2\text{O}_4$  and determine its solubility in hot water, 6*n*  $\text{HAc}$  and *n*  $\text{HCl}$ .

**6. Additional Precipitates of Strontium-ion.**—Strontium phosphate,  $\text{SrHPO}_4$  or  $\text{Sr}_3(\text{PO}_4)_2$ , white; strontium sulfite,  $\text{SrSO}_3$ , white. This last precipitate is slightly soluble in excess  $\text{H}_2\text{SO}_3$ , forming the bisulfite.

**7. Flame Test.**—Make a flame test with the nitrate solution containing a few drops of  $\text{HCl}$ , or with  $\text{SrCl}_2$ . Compare the flame with Plate IV, *B*.

### EXERCISES

1. Suppose that you have a solution containing  $\text{Ba}^{++}$  and  $\text{Sr}^{++}$ . Under what conditions could you precipitate  $\text{BaCrO}_4$  from the solution and not  $\text{SrCrO}_4$ ?

2. Is it possible to precipitate both chromates from the same solution and at the same time?

3. If we are to precipitate with a saturated solution of  $\text{CaSO}_4$ , is there any general rule that might be given for the concentration of the solution to which the  $\text{CaSO}_4$  is added?

4. You are given a mixture of  $\text{BaSO}_4$  and  $\text{SrSO}_4$ . Outline a scheme for the separation of  $\text{Ba}^{++}$  from  $\text{Sr}^{++}$ .

### CALCIUM-ION, $\text{Ca}^{++}$ (COLORLESS)

**1. Calcium Carbonate,  $\text{CaCO}_3$ .**—Precipitate 3 cc. test solution of  $\text{Ca}(\text{NO}_3)_2$  by first making ammoniacal, then adding  $(\text{NH}_4)_2\text{CO}_3$  in excess. Settle, decant and wash once with water. Test the solubility of  $\text{CaCO}_3$  in  $6n$   $\text{HAc}$ ,  $n$   $\text{HCl}$ ,  $\text{NH}_4\text{Cl}$  and hot water.

**2. Calcium Hydroxide,  $\text{Ca}(\text{OH})_2$ .**—Try to precipitate  $\text{Ca}(\text{OH})_2$  by taking a test solution of  $\text{Ca}(\text{NO}_3)_2$  and adding  $\text{NH}_4\text{OH}$ . If no precipitate results, use more concentrated solutions of each substance. Add  $\text{NaOH}$  solution to a test solution of  $\text{Ca}(\text{NO}_3)_2$ . Explain results.

**3. Calcium Sulfate,  $\text{CaSO}_4$ .**—Precipitate  $\text{CaSO}_4$  in as many ways as you are able and compare the physical appearances of the precipitates. With  $\text{BaSO}_4$  and  $\text{SrSO}_4$  as a basis, make a forecast of the solubilities of  $\text{CaSO}_4$  in  $6n$   $\text{HAc}$ ,  $n$   $\text{HCl}$ , strong  $\text{NH}_4\text{Cl}$  and hot water; then try the experiments. Is the sulfate prepared with an ammonium salt the same as the one prepared by using  $\text{K}_2\text{SO}_4$  as the precipitating agent?

**4. Calcium Chromate,  $\text{CaCrO}_4$ .**—Outline your own tests to determine whether  $\text{CaCrO}_4$  is more like  $\text{BaCrO}_4$  or  $\text{SrCrO}_4$  in solubilities.



**5. Calcium Oxalate,  $\text{CaC}_2\text{O}_4$ .**—Precipitate  $\text{CaC}_2\text{O}_4$  from an ammoniacal solution of  $\text{Ca}(\text{NO}_3)_2$  by adding  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  in excess. Settle, decant and wash once with water. Test the solubility in  $6n$   $\text{HCl}$ ,  $n$   $\text{HCl}$  and hot water. Boil a suspension of  $\text{CaC}_2\text{O}_4$  and then set aside for some time. Do the finely divided particles slowly change to needle-like crystals? Explain.

**6. Additional Precipitates of Calcium-ion.**—Calcium phosphate,  $\text{CaHPO}_4$  or  $\text{Ca}_3(\text{PO}_4)_2$ , white; calcium-potassium ferrocyanide,  $\text{CaK}_2[\text{Fe}(\text{CN})_6]$ , white; calcium sulfite,  $\text{CaSO}_3$ , white. This last precipitate is very soluble in excess  $\text{H}_2\text{SO}_3$ , forming the bisulfite ion  $\text{HSO}_3^-$ .

**7. Flame Test.**—Make a flame test, using  $\text{CaCl}_2$ , and compare with Plate IV, *C*. How does the flame differ from that of  $\text{Na}$ ?

### EXERCISES

1. Compare the physical appearances and the solubilities of the carbonates of barium, strontium and calcium.

2. Obtain first the  $K_{\text{SP}}$  for  $\text{Ca}(\text{OH})_2$ . Next calculate the  $(\text{OH}^-)$  in  $0.1m$   $\text{NH}_4\text{OH}$ . Substituting this value in the  $K_{\text{SP}}$ , calculate the  $[\text{Ca}^{++}]$  necessary to begin precipitation. How does this value compare with that of a saturated solution of  $\text{Ca}(\text{NO}_3)_2$ ? Conclusion?

3. We have found that precipitates containing the alkaline-earth group radicals may consist of chromates, sulfates, hydroxides and oxalates, as well as carbonates. Outline what you think are possible procedures if the group were precipitated in the form of each of the above instead of carbonates. For example, use  $\text{K}_2\text{CrO}_4$  as the group reagent and state what would be the necessary conditions for precipitation, also the completeness of precipitation and how you would proceed with a subsequent analysis.

4. Devise an experiment based upon your preliminary tests, to show what is meant by fractional precipitation.

5. How would you proceed to determine whether a  $\text{SrSO}_4$  precipitate is contaminated with  $\text{CaSO}_4$ ?

6. Suppose  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$  have been dissolved in  $\text{HCl}$ . How would you reprecipitate the group as carbonates? How would you reprecipitate the group as sulfates?

7. The carbonates of the group are dissolved in  $6n$   $\text{HCl}$ . If we now add  $\text{K}_2\text{CrO}_4$ , what will be the result?

8. Why not precipitate the carbonate group by adding  $\text{Na}_2\text{CO}_3$ ?

## PLATE IV

### FLAME TESTS

To make a platinum wire flame test, the wire is first cleaned by alternately dipping in 12*n* HCl and strongly heating in a non-luminous gas flame. When no color is imparted to the flame, the wire is touched to the solid which has been moistened with 12*n* HCl or dipped in a few drops of a solution which has been concentrated and one drop of 12*n* HCl added. The wire is carefully brought into the side of the oxidizing flame at *C*, shown in Fig. 8.

A. The characteristic grayish-green flame of barium. The flame is not a brilliant green as a rule, probably due to sodium contamination.

B. The crimson flame of strontium is very characteristic but is not made satisfactorily from a dilute solution notwithstanding the intensity of the flame. Some have the impression that because the crimson of strontium is very intense it should be obtainable from a dilute solution. It is a fact that it is intense when produced, but the solution must be of sufficient concentration before any test is obtained.

C. The characteristic flame for calcium is orange-red but it is more usually an orange-yellow due to sodium contamination. The flame is not very satisfactory in the identification of calcium.

D. The intense yellow flame of sodium. This flame is usually very persistent but sometimes in the analysis of unknowns it remains for a moment only.

E. The violet-blue flame of potassium is usually obscured by sodium contamination or other flames and should be viewed through a cobalt glass flame screen to shut out conflicting wave lengths.

F. The flame of copper is usually mentioned as blue but when made with salts and solutions from laboratory stock bottles it is decidedly green. The explanation may be that the sodium flame which is ever present furnishes sufficient yellow wave lengths that together with the blue of copper give a green color effect. Pure copper when volatilized and the vapor then heated to incandescence gives a blue flame but in qualitative analysis we are dealing with solutions and not the vapor from a pure metal.

# PLATE IV



A

B

C



D

E

F



## SUMMARY OF REACTIONS OF THE IONS IN GROUP IV THAT ARE OF IMPORTANCE IN ANALYTICAL PROCEDURE

Since the three members of the alkaline-earth group have solubility characteristics which differ more in moderate degrees than in extreme differences, it is evident that it will be necessary to make separations with the acidity, alkalinity and concentration under careful control.

The carbonates are the most insoluble for the entire group and  $(\text{NH}_4)_2\text{CO}_3$  is selected as the group reagent. The solution is made alkaline because we have found that the carbonates are very soluble in acids, even with 6*n* acetic acid. The sulfates as a group precipitate are not to be considered on account of the high solubility of  $\text{CaSO}_4$  which is 0.2 grams in 100 cc. of solution. Again, the question of dissolving the sulfates would add to the difficulty of the procedure.

In the preceding three groups we have first taken the group precipitate and added a solvent which would remove a part of the group, thus leaving a residue and a filtrate for further analysis. In the carbonate group this is impossible because there is no solvent that will readily dissolve only part of the group precipitate. The second method, therefore, for the general analysis of a group precipitate is followed. This consists in dissolving the group precipitate and then adding a reagent that will precipitate one or more of the radicals in solution. This group will be dissolved in warm 6*n* acetic acid.

The chromate of barium is much more insoluble in acetic acid than those of strontium or calcium, and we are able to separate barium by adding potassium chromate. The carbonates of strontium and calcium, after neutralizing the excess of acetic acid, are reprecipitated in order to remove the excess of  $\text{K}_2\text{CrO}_4$  which can be washed out of the carbonate precipitate. The presence of a large excess of chromate-ion would interfere with subsequent precipitations.

To separate strontium from calcium, the greater insolubility of strontium sulfate is made use of. The addition of  $\text{K}_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  can be used for precipitating the  $\text{SrSO}_4$ , or, where the solution is concentrated to a small volume, the addition of a saturated solution of  $\text{CaSO}_4$  will cause the precipitate to form.

Calcium is generally precipitated in the filtrate from the sulfate



separation by adding  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . Calcium oxalate is very insoluble, but it must be remembered that it is sometimes slow in forming.

In the alkaline-earth group separations, ample time must be allowed for the precipitates to form. A precipitate may be very insoluble, but if it takes several hours to come out thoroughly, the amount of solid which can be obtained in one hour will correspond to that of a comparatively soluble substance. Colloidal suspensions also give trouble in this group, and in order to obtain satisfactory results the precipitating may be carried out in hot solution or it may be possible to make the precipitate settle out by careful warming.

Confirmatory tests are indispensable for each of the three radicals. For example, where there is a large amount of calcium present and very little strontium, the former will precipitate in considerable quantity together with the  $\text{SrSO}_4$ . In fact, where no  $\text{SrSO}_4$  is precipitated by the addition of the soluble sulfate, there may be a good precipitate of  $\text{CaSO}_4$ . Without confirmatory tests, this might lead one to infer that strontium was present.

#### PROCEDURE FOR THE ANALYSIS OF A PRACTICE SOLUTION CONTAINING GROUP IV

The filtrate from the  $(\text{NH}_4)_2\text{S}$  group is supposed to have been made acid with acetic acid, concentrated to 20 cc., cooled, any free S removed by filtering and the solution reserved for this group.<sup>a</sup> Upon standing, crystals of  $\text{NH}_4\text{Cl}$  may appear, and they should be filtered off.<sup>b</sup> The solution to be used for Group IV, which either results as the filtrate from Group III, or is a practice solution of this group only must be perfectly clear<sup>c</sup> before the group reagent is added.

**Precipitation of the Group.**—Add 10 cc. 3*n*  $\text{NH}_4\text{Cl}$  to the solution, unless it is the filtrate from Group III, in which case the  $\text{NH}_4\text{Cl}$  will already be present. Make ammoniacal with  $\text{NH}_4\text{OH}$ , heat nearly to boiling<sup>d</sup> and add 10 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent.<sup>e</sup> Close the flask with a cork stopper and place in warm water for at least one hour<sup>f</sup> to permit the precipitate to settle. Decant the liquid through filter paper, wash once with cold water and again decant through the paper. If the settling process has continued long enough, most of the precipitate will form an incrustation<sup>g</sup> on the

inside of the flask. Wash once with cold water and pour washings through filter paper. Reserve filtrate for next group, if present.

**Dissolving the Group Precipitate.**—Add 10 cc. 6*N* HAc to the flask and carefully warm over a flame until the carbonates are dissolved. Pour this hot solution through the filter paper<sup>h</sup> previously used in the decantation, wash the flask once with hot water and pour the wash water also through the filter paper.

**Separation and Identification of Barium.**—Make a side test for barium by taking 1 cc. of the acetates in a test tube, dilute with 3 cc. water, heat to boiling and add, dropwise, not over 5 drops  $\text{K}_2\text{CrO}_4$  solution. Yellow  $\text{BaCrO}_4$  indicates barium. If the presence of barium has been shown, add this side-test solution to the main acetate solution and precipitate all of the  $\text{BaCrO}_4$  as you did in the side test.<sup>i</sup> Filter and wash once with hot water. Where the precipitation has been carried out as just outlined, it is practically impossible for the precipitate to consist of anything but  $\text{BaCrO}_4$ . A flame test for barium can be made by taking a clean platinum wire, moistening in concentrated HCl, dipping in the precipitate and holding in the flame. The characteristic **green flame** for barium should appear even though there is a slight contamination with strontium.

**Reprecipitation of  $\text{SrCO}_3$  and  $\text{CaCO}_3$ .**—Add  $\text{NH}_4\text{OH}$  or  $\text{NaOH}$  in slight excess to the filtrate containing the acetates and chromates of strontium and calcium. Next precipitate with  $(\text{NH}_4)_2\text{CO}_3$  in a flask as you previously did for the entire group. Give plenty of time to settle because there is usually very little precipitate at this point and it may otherwise be lost. Decant through filter paper, wash and reject filtrate and washings.<sup>j</sup>

**Separation and Identification of Strontium.**—Dissolve  $\text{SrCO}_3$  and  $\text{CaCO}_3$  in HAc as you did the original group, and finally pour the solution of acetates through the filter paper. Wash the flask once with 4 cc. water and pour the washings through the filter paper. Concentrate the acetates to about 5 cc., cool, make alkaline with  $\text{NH}_4\text{OH}$  and precipitate with 5 cc.  $(\text{NH}_4)_2\text{SO}_4$ . Settle and filter.<sup>k</sup> Wash the white  $\text{SrSO}_4$ , which indicates the presence of strontium, once with water. Confirm strontium by dipping a clean platinum wire in concentrated HCl, then in the  $\text{SrSO}_4$ , and holding in the flame. The **crimson flame** confirms strontium.

**Precipitation and Identification of Calcium.**—Concentrate the filtrate from the  $\text{SrSO}_4$  separation to about 2 cc.,<sup>l</sup> cool, make ammoni-

acal and add 2 cc.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  reagent. Set aside if a precipitate does not form immediately. A white precipitate indicates  $\text{CaC}_2\text{O}_4$ , the test for calcium. Confirm by adding concentrated HAc in which the white  $\text{CaC}_2\text{O}_4$  is insoluble.<sup>m</sup> An additional flame test can be made as with  $\text{SrSO}_4$  and the **orange-red** will confirm calcium.

#### NOTES ON THE PROCEDURE FOR THE ANALYSIS OF GROUP IV

a. As previously discussed, the formation of  $\text{SO}_4^-$  would prematurely precipitate a part at least of Group IV as sulfates. The carbonate must be precipitated in concentrated solutions. They could be precipitated finally in dilute solutions but it would require several hours.

b. The presence of  $\text{NH}_4\text{Cl}$  is necessary to prevent the precipitation of  $\text{Mg}(\text{OH})_2$  in this group. A large excess is undesirable, however, because later in Group V it must be completely removed by ignition, and besides, when concentrated, it has a solvent effect upon the carbonates.

c. A clear solution should always be used in precipitation so that the formation of a precipitate can be definitely noted. If a sediment is carelessly overlooked before the reagent is added and after the addition has been made a slight precipitate appears, the impression will be that the group is present although no confirmatory tests will later be obtained. About the only exception to this rule is in the precipitation of the  $\text{H}_2\text{S}$  group where oxy-compounds may be allowed.

d. The solution is quickly heated nearly to boiling. It is evident that if the heating is continued over a long interval of time most of the  $\text{NH}_4\text{OH}$  will be driven off.

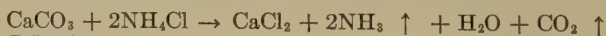
e. In order to precipitate the carbonate group it is necessary to have the reagent free from bicarbonate because the bicarbonates of barium, strontium and calcium are soluble. A high grade of  $(\text{NH}_4)_2\text{CO}_3$  should be used, and when prepared with excess  $\text{NH}_4\text{OH}$  any bicarbonate which might be present is changed to the carbonate as shown in the following:



Since both radicals present in ammonium carbonate are from a weak base and a weak acid, it follows that a water solution will readily hydrolyze. Excess  $\text{NH}_4\text{OH}$  will also reduce this, as shown in:



f. This settling process should be carried out irrespective of the amount of precipitate that is immediately formed. Unless this group is very completely removed it will offer a difficulty in the next group in connection with the phosphate test for magnesium. Do not boil the precipitate in the presence of  $\text{NH}_4\text{Cl}$ . The following equation shows how a solvent action will result:



g. Since the carbonates may be very finely divided when first formed and would pass through the filter, this characteristic scale or crust formation inside the flask is of great assistance. Do not attempt to remove it, but add acetic acid directly to the flask. By rotating the flask a little the entire sediment can readily be put into solution.

h. This will also dissolve any carbonate that may have been carried into the paper during decantation.

i. All of the barium must be removed before sulfate ions are added because  $\text{BaSO}_4$  will also precipitate and interfere with the  $\text{SrSO}_4$  test. Roughly approximate the proper dilution to be made so that the concentration will correspond to that used in the side test for  $\text{BaCrO}_4$ . Proper dilution and acidity preclude the possibility of  $\text{SrCrO}_4$  and  $\text{CaCrO}_4$  precipitating.

j. The filtrate and washings are discarded here because they contain principally the excess  $\text{K}_2\text{CrO}_4$ . The filtrate should have a light yellow color showing a slight excess of  $\text{K}_2\text{CrO}_4$ . Washing the carbonates once will remove this slight excess of chromate.

k. Here again, the solution must be concentrated. The finely divided  $\text{SrSO}_4$  will not readily separate from a dilute solution. If strontium goes through to the filtrate which is supposed to contain only calcium, it will later be precipitated as  $\text{SrC}_2\text{O}_4$  which is white like that of  $\text{CaC}_2\text{O}_4$ .

l. A high concentration was never more necessary than here. Many times in making this test, if the test tube is one-half full of solution no results whatever can be obtained. If the solution is concentrated to one-fourth this volume a slight turbidity will be formed, while if the concentration is carried down to 2 cc. an instantaneous precipitate will result. The calcium oxalate test cannot be made in a dilute solution.

m. This solubility test is difficult to make. The solubilities of  $\text{SrC}_2\text{O}_4$  and  $\text{CaC}_2\text{O}_4$  are not great and the solubility of either in  $\text{HAc}$  is not so great that one will dissolve instantly and the other will not. It is a worthless procedure to decide that a precipitate is  $\text{SrC}_2\text{O}_4$  and not  $\text{CaC}_2\text{O}_4$  because on adding 10 drops of concentrated  $\text{HAc}$  complete solution occurs. Where the amount of precipitate can vary through wide limits, the best way to establish a standard set of conditions is to shake up the 4 cc. of solution containing the oxalate precipitate, pour 1 cc. of the suspension into another test tube and add to the 1 cc. exactly 10 drops of very concentrated  $\text{HAc}$  which is kept especially for this purpose. Under these conditions the  $\text{SrC}_2\text{O}_4$  will usually dissolve and the  $\text{CaC}_2\text{O}_4$  will not. Even with these conditions, however, a slight turbidity may remain with the  $\text{SrC}_2\text{O}_4$ , but the result is sufficiently different from that obtained with  $\text{CaC}_2\text{O}_4$  to permit a distinction to be made.

#### OPTIONAL TESTS IN THE ANALYSIS OF GROUP IV

Magnesium can be precipitated in Group IV by not having  $\text{NH}_4\text{Cl}$  present when  $(\text{NH}_4)_2\text{CO}_3$  is added to the ammoniacal solution. This requires, however, that  $\text{NH}_4\text{Cl}$  be omitted in the procedure when Group III is precipitated. If  $\text{NH}_4\text{Cl}$  were added in Group III it would necessarily be present in the filtrate used for Group IV. It is generally considered that the alkaline-earth group is difficult enough without adding magnesium to it. Moreover, if



$\text{NH}_4\text{Cl}$  is omitted when Group III is precipitated, there is the danger of having a part of the  $\text{Mg}(\text{OH})_2$  also precipitated in that group.

The removal of excess  $\text{K}_2\text{CrO}_4$  can be omitted where a very light color shows it to be in slight excess only. It is difficult to reprecipitate  $\text{SrCO}_3$  and  $\text{CaCO}_3$ , especially if they are present in small amounts.

Strontium can be precipitated by adding  $\text{K}_2\text{SO}_4$ . The solution should then be warmed, or perhaps brought to a boil, in order to promote the solution of  $\text{CaSO}_4$  which is also present. Where  $(\text{NH}_4)_2\text{SO}_4$  is used there is formed a double salt of calcium which greatly aids in putting calcium into the filtrate and is shown by the following:



The use of alcohol to increase the insolubility of the carbonates, sulfates and oxalates is only satisfactory where the solutions are concentrated and the alcohol is very strong. As soon as the alcohol has absorbed much moisture from the air, its precipitating value is gone, and it will actually retard precipitation by dilution.



## PROCEDURE SHEET VIII

## ANALYSIS OF GROUP IV

Final tests are underscored twice

Fifteen cubic centimeters practice solution contains  $\text{Ba}^{++}$ ,  $\text{Sr}^{++}$  and  $\text{Ca}^{++}$ . Add 10 cc.  $3n$   $\text{NH}_4\text{Cl}$ , unless solution is filtrate from Group III in which case the  $\text{NH}_4\text{Cl}$  is already present. Make ammoniacal with  $\text{NH}_4\text{OH}$ , heat nearly to boiling, then add 10 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent. Settle for one hour in a warm water bath. Decant through filter paper, wash once with cold water and decant washings through filter paper.

Precipitate: <u><math>\text{BaCO}_3</math></u> , <u><math>\text{SrCO}_3</math></u> , <u><math>\text{CaCO}_3</math></u> . Dissolve precipitates in 10 cc. $6n$ $\text{HAc}$ . Make side test for $\text{Ba}^{++}$ , and if present dilute with water, heat nearly to boiling and add $\text{K}_2\text{CrO}_4$ in slight excess. Filter and wash once with hot water.	Filtrate: Succeeding group, if present.
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Precipitate: <u><math>\text{BaCrO}_4</math></u> , yellow. Confirm by making flame test. <u>Green flame.</u>	Filtrate: $\text{Sr}^{++}$ , $\text{Ca}^{++}$ and excess $\text{K}_2\text{CrO}_4$ . Add $\text{NH}_4\text{OH}$ or $\text{NaOH}$ in slight excess, then reprecipitate with $(\text{NH}_4)_2\text{CO}_3$ . Filter and wash once with cold water.
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Precipitate: <u><math>\text{SrCO}_3</math></u> , <u><math>\text{CaCO}_3</math></u> . Dissolve in warm $\text{HAc}$ , concentrate to 5 cc., cool, make ammoniacal and add 5 cc. $(\text{NH}_4)_2\text{SO}_4$ reagent. Settle and filter, Wash once with cold water.	Filtrate: Reject.
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Precipitate: White <u><math>\text{SrSO}_4</math></u> . Confirm by <u>crimson flame test.</u>	Filtrate: $\text{CaSO}_4$ or $\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2$ . Concentrate to 2 cc., cool, make ammoniacal and add 2 cc. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ reagent. White <u><math>\text{CaC}_2\text{O}_4</math></u> indicates calcium. Confirm by adding conc. $\text{HAc}$ in which it <u>does not dissolve.</u>
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## CHAPTER VII

### GROUP V.—MAGNESIUM AND THE ALKALI RADICALS

MAGNESIUM, Mg: at. wt. 24.32:  $Mg^{++}$

POTASSIUM, K: at. wt. 39.096:  $K^+$

SODIUM, Na: at. wt. 22.99:  $Na^+$

AMMONIUM,  $NH_4$ : .....:  $NH_4^+$

This group consists of cations of the alkali metals, ammonium and magnesium. Since they appear so late in a systematic procedure of analysis, it is evident that the majority of compounds containing these radicals have a high solubility. This group is not precipitated as customarily by a group precipitating agent but is analyzed by making individual tests for its members.

#### MAGNESIUM-ION, $Mg^{++}$ (COLORLESS)

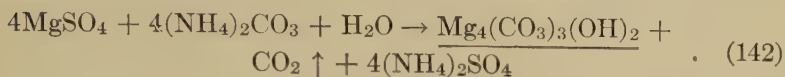
**1. Magnesium Hydroxide,  $Mg(OH)_2$ .**—Add  $NH_4OH$  in excess to 3 cc. test solution of  $Mg(NO_3)_2$ . The white gelatinous precipitate is  $Mg(OH)_2$ . Take one-half of this solution and its precipitate, heat to boiling and then set aside. Does the precipitate change upon standing? To the other half, add a large excess of  $NH_4OH$ . Does it redissolve?

Precipitate another portion of  $Mg(OH)_2$  in a test solution of  $Mg(NO_3)_2$  by adding  $NH_4OH$  in excess and then add  $NH_4Cl$ . Does the precipitate dissolve? Try the effect of boiling. Check your result by adding  $NH_4Cl$  to a test solution of  $Mg(NO_3)_2$  and then adding  $NH_4OH$ . Would the result be the same were you to use  $NH_4Cl$  and then add  $NaOH$ ? Try the experiment if you are not sure of your answer.

**2. Magnesium Carbonate,  $MgCO_3$ .**—Precipitate two portions of  $MgCO_3$  by adding  $(NH_4)_2CO_3$  and  $Na_2CO_3$  as the reagents. Now add  $NH_4Cl$  in excess to each. Does solution result in either case? Repeat by adding  $NH_4Cl$  before the reagents.

Interpret the results. You must clearly distinguish in these tests the difference between the common-ion effect of  $\text{NH}_4\text{Cl}$  upon ammonium compounds and the absence of the common-ion effect when other ammonium compounds are not present.

Basic magnesium carbonates are frequently precipitated by  $(\text{NH}_4)_2\text{CO}_3$  in the absence of ammonium salts. One of the possible reactions is:



**3. Magnesium Acid Phosphate,  $\text{MgHPO}_4$ , and Magnesium Ammonium Phosphate,  $\text{MgNH}_4\text{PO}_4$ .**—Add  $\text{Na}_2\text{HPO}_4$  to a neutral test solution of  $\text{Mg}(\text{NO}_3)_2$ . The white precipitate is  $\text{MgHPO}_4$ . Write the equation. Repeat the experiment by adding  $\text{NH}_4\text{OH}$  to the test solution until ammoniacal, then add a few crystals of  $\text{NH}_4\text{Cl}$ . After complete solution of the crystals, add  $\text{Na}_2\text{HPO}_4$  reagent. The crystalline precipitate is  $\text{MgNH}_4\text{PO}_4$ . If the solution is quite concentrated the precipitate may be quite flocculent at first. The larger well-formed crystals will result slowly only in a more dilute solution. Take a dilute solution and after adding the precipitating reagent, set aside for crystal formation. Test the solubility of  $\text{MgNH}_4\text{PO}_4$  in  $6n$   $\text{HAc}$ . The high solubility of this precipitate even in acetic acid will distinguish it from other phosphates.

**4. Magnesium Oxalate,  $\text{MgC}_2\text{O}_4$ .**—Add  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  to a test solution of  $\text{Mg}(\text{NO}_3)_2$ . Concentrate the solution if no precipitate appears. Is the oxalate as satisfactory a precipitate as magnesium ammonium phosphate for the identification of  $\text{Mg}^{++}$ ?

### EXERCISES

1. After referring to the solubility tables, decide whether  $\text{Mg}(\text{OH})_2$  can be precipitated from a solution of  $\text{Mg}(\text{NO}_3)_2$  by adding a suspension of  $\text{Ca}(\text{OH})_2$ . Answer the same question for a suspension of  $\text{Ba}(\text{OH})_2$ .

2. How does the base-forming character of  $\text{MgO}$  compare with that of the oxides of barium, strontium and calcium? Upon what do you base your answer?

3. Make a list of the water-soluble salts of magnesium.

4. When ammonium carbonate is added to the filtrate which is to be used for Group IV and which contains soluble magnesium salts, why is not magnesium precipitated as the hydroxide? As the carbonate?

5. Will the filtrate from a  $\text{MgHPO}_4$  precipitate be precipitated by the addition of  $\text{NH}_4\text{Cl}$ ?

POTASSIUM-ION,  $K^+$  (COLORLESS)

The salts of potassium, sodium and ammonium are quite uniformly soluble in water so that the list of precipitates containing these radicals is very limited.

**1. Potassium Chloroplatinate,  $K_2PtCl_6$ .**—Add, dropwise, to 3 cc. test solution of  $KNO_3$  not over 5 drops  $H_2PtCl_6$  reagent. The light yellow crystalline precipitate is  $K_2PtCl_6$ . Add 4 drops 95 per cent alcohol if the precipitate forms slowly. Dissolve one-half of the precipitate in an excess of  $NaOH$ . Test the solubility of the other half with  $12n$   $HCl$ . What are the proper conditions for precipitating  $K_2PtCl_6$ ?

**2. Potassium-sodium Cobaltinitrite,  $K_2Na[Co(NO_2)_6]$ .**—Add to a test solution of  $KNO_3$ , acidified with 3 drops of  $HAc$ , 1 cc. sodium cobaltinitrite reagent. The orange-yellow precipitate is mostly  $K_2Na[Co(NO_2)_6]$ , although there may be some  $K_3[Co(NO_2)_6]$  present as well. This reagent readily decomposes and as such is useless in the test. It is necessary, therefore, to test the reagent at frequent intervals. See Plate I, *K* and *L*, for a comparison of the colors of the precipitates  $K_2PtCl_6$  and  $K_2Na[Co(NO_2)_6]$ .

**3. Potassium Acid Tartrate,  $KHC_4H_4O_6$ .**—Add sodium acid tartrate solution to 3 cc. test solution of  $KNO_3$ . Stir with a glass rod to promote the formation of crystals. Test the solubility of some of the  $KHC_4H_4O_6$  in  $6n$   $HCl$ . Why is the acid tartrate better than tartaric acid as the precipitating reagent?

**4. Potassium Perchlorate,  $KClO_4$ .**—Add 3 cc. strong ethyl alcohol to 3 cc. test solution of  $KNO_3$ , then add, dropwise, not over 20 drops of perchloric acid reagent. Describe the precipitation of the  $KClO_4$  which forms.

**5. Flame Test.**—Make a flame test, using  $KCl$  solution or that of another salt to which a drop of concentrated  $HCl$  has been added. Use the cobalt-blue glass screen to shut off interfering wave lengths. Compare the flame with that on Plate IV, *E*.

## EXERCISES

**1.** Which of the following statements do you think correct? (a) In a saturated  $KCl$  solution, or in 75 per cent alcohol, the  $K_2PtCl_6$  precipitate is practically insoluble.

(b) Hydrochloroplatinic acid ( $H_2PtCl_6$ ) produces, in neutral concentrated acid solutions of potassium salts, a yellow crystalline precipitate of potassium chloroplatinate ( $K_2PtCl_6$ ).

(c) Hydrochloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) added to a neutral or strongly acid solution of a potassium salt, gives a yellow crystalline precipitate of potassium chloroplatinate ( $\text{K}_2\text{PtCl}_6$ ).

2. How, in general, are acid salts prepared?
3. Is the acid salt always more insoluble than the normal one? Give examples.
4. In what other test has  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$  been precipitated?

#### SODIUM-ION, $\text{Na}^+$ (COLORLESS)

**1. Sodium Chloroplatinate,  $\text{Na}_2\text{PtCl}_6$ .**—Prepare a solution of  $\text{Na}_2\text{PtCl}_6$  in a manner similar to that used for the preparation of  $\text{K}_2\text{PtCl}_6$ . No precipitate should form even when a high concentration of sodium salt is used. See if the addition of alcohol causes precipitation.

**2. Sodium Cobaltinitrite,  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ .**—This, of course, does not precipitate because we used it in solution in the potassium test.

**3. Sodium Acid Antimonate,  $\text{NaH}_2\text{SbO}_4$ .**—Add to 2 cc. of a test solution of  $\text{NaCl}$  an equal volume of  $\text{KH}_2\text{SbO}_4$  reagent. A white precipitate of  $\text{NaH}_2\text{SbO}_4$  will form if the solution of the sodium salt is sufficiently concentrated and the reagent is correctly prepared. The solution in which the test is made must be alkaline with  $\text{KOH}$ , otherwise antimonious acid,  $\text{H}_3\text{SbO}_4$ , will be precipitated.

**4. Flame Test.**—A very brilliant yellow flame indicates sodium (see Plate IV, *D*). The test is an exceedingly delicate one and traces of sodium compounds are likely to be obtained in nearly all solutions unless non-soluble glass is used. Where sodium is a contamination, the flame will be a dull yellow and not so persistent.

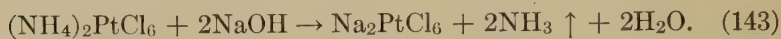
#### EXERCISES

1. What is an alkali? Make a list of alkalies.
2. Alkalies have been classified as fixed and volatile. What is the difference?
3. Test solutions of  $\text{NaCl}$  and  $\text{NH}_4\text{Cl}$  with neutral litmus. Explain any differences.
4. Sodium hydroxide, when heated with zinc dust, liberates hydrogen. Where does the hydrogen come from? Can you see any suggestion of the acid character of  $\text{NaOH}$  in this reaction?



AMMONIUM-ION,  $\text{NH}_4^+$  (COLORLESS)

**1. Ammonium Chloroplatinate,  $(\text{NH}_4)_2\text{PtCl}_6$ .**—Test a solution of  $\text{NH}_4\text{Cl}$  with  $\text{H}_2\text{PtCl}_6$  as you did with the potassium-ion. Is the precipitate of  $(\text{NH}_4)_2\text{PtCl}_6$  any different from a similar one of potassium? Can this test for potassium be made in the presence of ammonium salts? Decant the liquid from the precipitate and add a few drops of strong  $\text{NaOH}$ . The reaction is:



How can the ammonium precipitate be distinguished from that of potassium?

**2. Ammonium Sodium Cobaltinitrite,  $(\text{NH}_4)_2\text{Na}[\text{Co}(\text{NO}_2)_6]$ .**—Prepare the precipitate and compare with a similar one with potassium-ion. How can the two be distinguished?

**3. Ammonium Acid Tartrate,  $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$ .**—The precipitate is similar to that of  $\text{KHC}_4\text{H}_4\text{O}_6$ .

**4. Ammonium Perchlorate,  $\text{NH}_4\text{ClO}_4$ .**—This salt is quite soluble and is an exception to the general similarity between the potassium and ammonium compounds.

**5. Sublimation and Decomposition of Ammonium Compounds by Heat.**—Place some  $\text{NH}_4\text{Cl}$  on a porcelain crucible cover and moisten with  $12n$   $\text{HNO}_3$ . Heat strongly with a gas burner. Can all of the ammonium salts be driven off? A certain amount of ammonium nitrate is formed and decomposes upon heating. The following shows one type of decomposition that may take place:

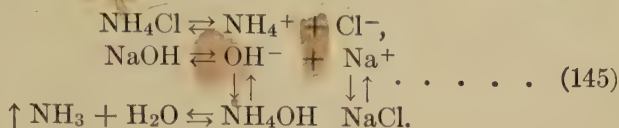


$\text{NH}_4\text{Cl}$  sublims when heated but requires a higher temperature than is necessary for the decomposition of the nitrate.

**6. The Decomposition of Ammonium Salts by  $\text{NaOH}$ .**—Place 3 cc. test solution of  $\text{NH}_4\text{Cl}$  in a small test tube fitted with a one-hole rubber stopper through which passes a glass bend. Add a small piece of solid  $\text{NaOH}$  to the solution, insert the stopper tightly and place a small piece of red litmus paper in the glass bend about  $\frac{1}{2}$  inch from the outer end. Do not plug the tube up with this paper but place it lengthwise of the tube. Now warm the tube and distill the  $\text{NH}_3$  over with steam. What change is there in the color of the litmus paper?

This is a reaction in which it is often erroneously stated

that a stronger base drives out a weaker one. The reaction is quite complete because of the elimination of one of the products, as will be seen from the following:



The four species of ions present are in equilibrium with four molecular species.  $\text{NH}_4\text{OH}$ , however, is in equilibrium with  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , and when the solution is heated the solubility of the gas,  $\text{NH}_3$ , is decreased so that it is quite completely eliminated. Since the equilibrium is constantly disturbed by the elimination of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , the  $\text{NH}_4\text{Cl}$  will be decomposed as long as there is an excess of  $\text{NaOH}$  and the solution is heated. Beginners often find it difficult to obtain a satisfactory test for  $\text{NH}_3$  unless the small distilling tube is used.

### EXERCISES

1. Do the ammonium salts have to be removed before the magnesium test is made?
2. When should the ammonium test be made in an analysis involving all of the groups?
3. Why are the ammonium salts changed as far as possible to nitrates before ignition?
4. Which of our preliminary tests can be used to distinguish  $\text{K}^+$  from  $\text{Na}^+$ ?  $\text{Na}^+$  from  $\text{NH}_4^+$ ?  $\text{K}^+$  from  $\text{NH}_4^+$ ?

### SUMMARY OF REACTIONS OF THE IONS IN GROUP V THAT ARE OF IMPORTANCE IN ANALYTICAL PROCEDURE

The tests for  $\text{Mg}^{++}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$  are so slightly related that separate portions of the filtrate from Group IV can be taken for individual tests. Salts of  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$  can be present when the  $\text{Mg}^{++}$  test is made. Magnesium is not precipitated as the hydroxide in the filtrate from Group IV because the presence of ammonium salts would make it incomplete. The precipitate of  $\text{MgNH}_4\text{PO}_4$  is the one usually used in the final identification of  $\text{Mg}^{++}$ . The conditions for making this test are that the solution be concentrated, ammoniacal and with no radicals of Groups I-IV present. The reagent  $\text{Na}_2\text{HPO}_4$  together with  $\text{Mg}^{++}$  will then give  $\text{MgNH}_4\text{PO}_4$ . To be certain that preceding metals are absent,

especially those of the alkaline-earth group, the solution to be used for the  $\text{Mg}^{++}$  test is reprecipitated with a few drops of  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . Any turbidity is filtered off, or boiled and then filtered off.

For the potassium test, all ammonium salts must be absent unless the perchloric acid test is to be used. To eliminate the ammonium salts, a part of the Group IV filtrate is evaporated to dryness, moistened with  $\text{HNO}_3$  and ignited. The residue, after being taken up with water and a few drops of  $\text{HCl}$ , can then be used for the test with  $\text{H}_2\text{PtCl}_6$  or  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ . The magnesium test can also be made in a part of the solution obtained after ignition. The hydroxide of magnesium will appear as soon as the solution is made ammoniacal because the ammonium salts have been removed.

The flame test in the original solution is usually used to identify sodium because the antimonate test will not give uniform results.

Where a flame test for potassium is to be made, any of the precipitates that contain  $\text{K}^+$  can be moistened with  $\text{HCl}$  and used in the test. Frequently a few drops of the original solution are evaporated nearly to dryness where analysis has shown that no interfering substance is present whose flame will obscure that of potassium.

The ammonium ion is always tested for in the original solution by the addition of  $\text{NaOH}$  as described in the preliminary tests.

#### PROCEDURE FOR THE ANALYSIS OF A PRACTICE SOLUTION CONTAINING GROUP V

**Preliminary Flame Test for Sodium and Potassium.**—Make a flame test in the original solution. An **intense yellow flame** indicates the presence of sodium in an amount greater than a trace. Use the blue cobalt glass and examine the flame for the presence of the **violet-blue flame** indicating potassium. If it appears to be present but the test is not altogether satisfactory, evaporate a few drops of the solution about to dryness, add 3 drops  $12n$   $\text{HCl}$  and use this for another flame test. There should be no question now<sup>a</sup> about the test.

**Identification of Ammonium-ion.**—Place 3 cc. of the original solution in a small test tube, add a small piece of solid<sup>b</sup>  $\text{NaOH}$  or

KOH, insert a tightly fitting one-hole rubber stopper<sup>c</sup> through which passes a glass bend containing in the outer end a loosely placed piece of red litmus paper<sup>d</sup>. Warm and if necessary boil gently<sup>e</sup>. **Red litmus changing to blue** indicates the presence of  $\text{NH}_4^+$ .

**Separation and Identification of Magnesium.**—Take one-third of the remaining solution and, if it is the filtrate from Group IV, add 1 cc. each of  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . Concentrate the solution to 3 cc., cool and filter off any precipitate<sup>f</sup> by using a double filter if necessary. Make the clear filtrate ammoniacal and then add 2 cc.  $\text{Na}_2\text{HPO}_4$  reagent. Set aside for one hour if the precipitate does not form immediately. The crystalline precipitate of  $\text{MgNH}_4\text{PO}_4$  indicates  $\text{Mg}^{++}$ , and it can be confirmed by dissolving in a few drops of strong  $\text{HAc}$ <sup>g</sup>.

**Identification of Potassium.**—Take the two-thirds portion of the main solution and boil down in an evaporating dish to about 3 cc. Cool, filter and place the clear filtrate in a porcelain crucible. Add 3 cc. 12*n*  $\text{HNO}_3$ , evaporate to dryness and ignite over a gas burner at a temperature not above that which will make the bottom of the crucible a dull red. Finally heat the sides of the crucible until no more white fumes are given off. Cool, add 2 cc. water and 3 drops 6*n*  $\text{HAc}$ , warm and stir with a glass rod. Filter, and to the clear filtrate add 5 drops 10 per cent  $\text{H}_2\text{PtCl}_6$  or 1 cc.  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  reagent. A yellow precipitate of  $\text{K}_2\text{PtCl}_6$  or of  $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$  indicates potassium<sup>h</sup>. In either case allow the solution to stand if the precipitate does not form immediately; with the  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  very slight warming is permissible.

#### NOTES ON THE PROCEDURE FOR THE ANALYSIS OF GROUP V

a. The preliminary flame test for potassium is very much worth while because it often happens that in subsequent ignition to get rid of all of the ammonium salts the heating may be overdone. In this way, the potassium salts may be largely volatilized.

b. With the small concentration of ammonium salts present in practice solutions, unless solid  $\text{NaOH}$  is added, the elimination of  $\text{NH}_3$  will not be satisfactory.

c. The apparatus must be very tight or the small amount of gas which is generated will be dissipated.

d. Use about  $\frac{1}{2}$  inch strip and fold lengthwise through the center. This v-shaped piece can now be pushed into the end of the tube without stopping it up. Push the paper in while it is dry. The steam coming out later will



moisten it. If the paper is about  $\frac{1}{4}$  inch inside the tube, there will be no danger of fumes in the room affecting it.

e. Where the test paper is placed on the bottom of a watch glass and held over the vapors, as is often directed, there is always danger of the alkaline solution spattering over the paper. If the litmus paper has not changed color by the time the steam is issuing from the tube, there is no necessity of heating any longer.

f. Since most phosphates are insoluble it is necessary that all metals in the preceding groups be removed. The alkaline-earth metals are especially troublesome at this point because they are frequently precipitated only in part on account of the group precipitation being hurried.

g. The precipitate of  $\text{MgNH}_4\text{PO}_4$  is so readily soluble in acids that it should dissolve at once when a few drops of 6*N* HAc are added. A persistent turbidity will indicate the presence of other phosphates. If there is still a question about magnesium being present, the turbid solution can be filtered and the clear filtrate made alkaline with  $\text{NH}_4\text{OH}$ . The magnesium phosphate will reprecipitate.

h. In going through this practice solution before unknowns are analyzed, it can be determined how much heating is necessary to drive off the ammonium salts but not those of potassium. A good check on the heating process can be made by taking a solution containing ammonium salts but not those of potassium. Now ignite and take up with acidulated water and make a test for potassium. If a precipitate forms with  $\text{H}_2\text{PtCl}_6$  or  $\text{Na}_2[\text{Co}(\text{NO}_2)_6]$ , insufficient ignition is indicated.

There is a decided personal factor in following any procedure, and tests like the one just given will prove how well the necessary conditions are being fulfilled.

#### OPTIONAL TESTS IN THE ANALYSIS OF GROUP V

The test for magnesium offers the only essential variation that can be made in the analysis of this group. The test can be made either before or after ignition. Each method has its advantages. Where it is made before ignition, there is no danger of losing volatile compounds by excessive heating. The solution must be concentrated and excess  $\text{NH}_4\text{Cl}$  removed by filtering. Where the solution is allowed to stand for some time after the addition of  $\text{NH}_4\text{OH}$  and  $\text{Na}_2\text{HPO}_4$ , there is always danger of  $\text{NH}_4\text{Cl}$  crystals forming and being mistaken for  $\text{MgNH}_4\text{PO}_4$ . After ignition there can be no difficulty from this source.



## PROCEDURE SHEET IX

## ANALYSIS OF GROUP V

Final tests are underscored twice.

Fifteen cubic centimeters practice solution contains  $\text{Mg}^{++}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$ . Make a flame test with original solution, or with a few drops evaporated about to dryness and moistened with  $\text{HCl}$ . Intense yellow flame, usually persisting for a few seconds, indicates sodium; characteristic violet flame obtained through cobalt glass is a preliminary test for potassium.

Place 3 cc. original solution in a small distilling tube and add a small piece solid  $\text{NaOH}$ . Warm and test vapor with red litmus paper. Change to blue indicates  $\text{NH}_4^+$ .

Take one-third remaining solution and reprecipitate, if preceding groups are present, by adding a few drops each of  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . Concentrate to 3 cc., cool, filter if turbid and discard precipitate. Make clear filtrate ammoniacal and add 2 cc.  $\text{Na}_2\text{HPO}_4$ .

Precipitate:  $\text{MgNH}_4\text{PO}_4$ . White, crystalline. Confirm by dissolving in a few drops of conc.  $\text{HAC}$ .

Filtrate:  
Discard.

Resume the two-thirds portion, concentrate to 3 cc. in evaporating dish, transfer to crucible, evaporate to dryness and ignite at dull red heat. Take up with 2 cc. water and 3 drops 6*N*  $\text{HAc}$ . Filter and test for  $\text{K}^+$  in clear filtrate, (1) adding 5 drops  $\text{H}_2\text{PtCl}_6$ , giving light yellow  $\text{K}_2\text{PtCl}_6$ ; or (2) adding 1 cc.  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ , giving orange-yellow  $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$ .

## CHAPTER VIII

### COMPLETE CATION ANALYSIS

#### PROCEDURE FOR THE ANALYSIS OF AN UNKNOWN SOLUTION CONTAINING ALL POSSIBILITIES OF CATION RADICALS FROM THE FIVE GROUPS, BUT WITH PHOSPHATES AND OTHER CONFLICTING RADICALS ABSENT

**Introduction.**—The analysis of a solution for the metallic radicals of all groups consists essentially in the combination of the five procedures just completed. There are, however, a few additional points to be considered on account of the groups succeeding each other instead of being contained in separate solutions. More details concerning certain points in the group procedures are also necessary.

**Preliminary Examination.**—The solution for analysis is usually received in a 25–30 cc. stoppered bottle or test tube and is numbered on a small label or preferably on the cork stopper. The numbers 6 and 9 are distinguished by underlining. As soon as you receive your unknown you should take the report sheet and record the number of the sample. A mistake in number is as serious as a complete miss in analysis. Make a preliminary examination for acidity and odor and also note the color of the solution and the presence of any sediment.

The solution will probably be neutral or acid to prevent the hydrolysis of certain salts. If it is alkaline and there is no sediment or precipitate present, the metallic radicals that can be present are very limited. Refer to a solubility table to determine the possibilities. The odor of ammonia will indicate the presence of ammonium hydroxide or the decomposition of an ammonium salt in the presence of a base.

Do not place too much importance upon the color of the solution. It is true that several ions have characteristic colors but when they are in combination, the colors may be neutralized some-

what, and an entirely different color produced. A yellow solution does not always indicate a chromate and instructors have means at their disposal to discourage the placing of undue emphasis upon the analysis of a solution by the colorimetric method.

A sediment in the solution usually results from the hydrolysis of compounds of antimony, bismuth or tin where the acidity has not been sufficiently great. A precipitate of  $\text{As}_2\text{O}_3$  may also be formed by the decomposition of arsenites, especially upon long standing. If  $\text{SnCl}_2$  is in the same solution with  $\text{SbCl}_3$  or  $\text{HgCl}_2$  a precipitate of Sb,  $\text{HgCl}$  or Hg will finally settle out. These are a few of the reactions that may result in the formation of a sediment in the sample. Fortunately, most of the solid matter involves radicals in Group II and this can be separated and analyzed without much difficulty.

A flame test should be made with the original solution or with a few drops which have been evaporated nearly to dryness. The preliminary identification of sodium is very definite, and, in the absence of sodium, very satisfactory flame tests can usually be obtained for strontium and barium. The preliminary flame test for calcium is unsatisfactory because, as pointed out in the section on flame tests, there is always the uncertainty whether calcium is present or an excess of sodium and a trace of strontium. This is especially unfortunate because the final test for calcium in Group IV may be very indefinite. The flame test for potassium is made through the flame screen and may be more conclusive than the one obtained in Group V where there is the conflict with ammonium salts and also the possible loss due to overheating.

The test for  $\text{NH}_4^+$  is always made during the preliminary examination of the solution, although, of course, it could be made at any time before ammonium salts have been added in the course of analysis.

**Analysis of Group I.**—Take one-half of the thoroughly mixed sample and, if there is a sediment present, filter and reserve the solid matter for Group II. It is very desirable to make side tests for the presence of the various groups so that the addition of the group reagent to the entire solution may be avoided if the group is not present. Take a few drops of the solution in a test tube and slowly add four drops of  $3n$  HCl. If the group is present, as shown by the formation of a white precipitate, add the test solution to the main solution and continue with the analysis of the group accord-

ing to Procedure Sheet I. If the group is absent add the test solution to the main solution and also add the sediment, if any was filtered off, by punching a hole in the filter paper and washing down with water.

What amounts to the same thing when a sediment is present is to filter a few drops for the test of the presence of the group. If present, then filter off the sediment, otherwise proceed to Group II without filtering.

**Analysis of Group II.**—Make a side test for the presence of Group II by taking 1 cc. of the solution and first adjust for  $0.3n$  HCl by means of acid cresol red (see Plate II, Q). Warm and pass  $H_2S$  through for two minutes. If the group is absent, discard the side test and pass to the analysis of Group III. If present, add the side test to the main solution, dilute to 100 cc. with water and test for the normality of the acid with acid cresol red. Adjust the acidity so that  $0.3n$  HCl is present. If you have precipitated Group I with HCl and added it in slight excess only, the filtrate will not be far from the correct acidity. Where the precipitation has been carelessly done, an adjustment will be necessary before the precipitation with  $H_2S$  is made or very unsatisfactory results will follow. If the indicator test shows greater acidity than  $0.3n$ , the solution can be diluted to more than 100 cc. to reduce the acidity.

Before precipitating with  $H_2S$ , preliminary tests should be made in separate small side tests for  $Fe^{++}$ ,  $Fe^{+3}$  and  $Hg^{++}$ . The potassium ferrieyanide, ferrocyanide and stannous chloride reagents are used for this purpose. These preliminary tests do not always give the desired information because there are several radicals that give precipitates with the cyanides, and the stannous chloride test is affected by the presence of strong oxidizing or reducing agents.

After precipitating Group II, remember to concentrate the filtrate and washings from the group precipitate, filter and set aside in a stoppered flask. Follow Procedure Sheets II, III and IV for the analysis of the group.

**Analysis of Group III.**—If the group is present, as shown by side test, analyze according to Procedure Sheets V, VI and VII, and remember to concentrate filtrate and washings from group precipitate to 20 cc. After cooling, filter off any turbidity through a double filter and set aside in a stoppered vessel.

**Analysis of Group IV.**—Make a preliminary test for the group and follow instructions in Procedure Sheet VIII.

**Analysis of Group V.**—Make the tests for magnesium and potassium as outlined in Procedure Sheet IX. The tests for sodium and ammonium have already been made.

**Checking up Results.**—It is a good plan, if there is not sufficient time to analyze completely the second half of the original solution, to make at least additional tests where the first analysis has given questionable results. For example, suppose that the test for calcium was not good, and no member of Group II was found to be present. You can now precipitate Group I with a little HCl in excess, filter off the precipitate and discard. Concentrate the filtrate, make ammoniacal with  $\text{NH}_4\text{OH}$  and in a side test determine the presence of Group III. If it is absent proceed directly to Group IV. If present, add  $\text{NH}_4\text{Cl}$ , precipitate with  $(\text{NH}_4)_2\text{S}$ , filter and discard precipitate. The ammonium carbonate group is now precipitated and we will suppose further that barium is absent. In this case you can dissolve the carbonate precipitate in acetic acid, make alkaline with  $\text{NH}_4\text{OH}$  and add the  $(\text{NH}_4)_2\text{SO}_4$  reagent for strontium. The addition of  $\text{K}_2\text{CrO}_4$  is, of course, unnecessary.

The main point to remember in checking an unsatisfactory test is that the particular place in the analytical scheme must be reached with the smallest number of operations. Every precipitation or solution weakens the intensity of succeeding tests because no precipitate is entirely insoluble.

**Reporting Results of Analysis.**—The radicals are reported together with their proper valences, and preferably in the order in which they occur in the analytical procedure, as  $\text{Hg}_2^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Ca}^{++}$ .

## A PROCEDURE REVIEW

The analysis of an unknown differs from that of the group practice solutions in that the unknown contains a limited number of radicals selected from all of the groups, while the group practice solution contains all of the radicals. It is evident that in the analysis of the unknown many of the steps are omitted and the omissions are self-evident to one who is familiar with the complete procedure.

Suppose, for example, we review the analysis of a solution containing silver, tin, calcium and ammonium ions. The preliminary



examination will show the solution to be clear, colorless and acid. The flame test will give a trace of sodium only. The preliminary test for ammonium will show the radical to be present. One-half of the solution is taken and the other half is set aside, carefully stoppered and labeled.

A side test with HCl shows the insoluble chloride group to be present. The test solution is added to the main solution and the group completely precipitated with  $3n$  HCl in slight excess. The white precipitate is filtered off, washed once with cold water containing a few drops of HCl and once with cold water. The filtrate and washings are reserved for Group II. The precipitate is extracted three times with the same hot water and finally washed once with a fresh amount of hot water, and the two solutions combined. The volume of precipitate appears to be about the same as before washing with hot water. One-half of the warm solution is made acid with a few drops of HAc, and  $K_2CrO_4$  is added dropwise. No precipitate results. To the other half,  $H_2SO_4$  is added and again there is no precipitate. We conclude that  $Pb^{++}$  is not present except as a trace.

Returning to the precipitate on the filter paper, we next pour over it about 1 cc.  $NH_4OH$ , and since there is no darkening we conclude that  $Hg_2^{++}$  is absent. Another cubic centimeter of  $NH_4OH$  completely dissolves the precipitate. The ammoniacal solution is now made acid with  $HNO_3$  and a white curdy precipitate, which darkens, especially at the edges, when heated, indicates  $Ag^+$ .

A side test has shown the presence of Group II, so the filtrate and washings from Group I are now diluted to 100 cc. with water and side tests made for  $Fe^{++}$ ,  $Fe^{+3}$  and  $Hg^{++}$  with negative results. We next make a side test, using about 2 drops, with acid cresol red which shows the acidity to be too low. We therefore add HCl until side tests show the normality to be  $0.3n$ . We return the side test solution for the group to the main solution, heat nearly to boiling and precipitate in a closed flask with  $H_2S$ . The precipitate is a yellowish-brown. We next cool the contents of the flask with tap water and filter, and, after the filtrate has been reheated,  $H_2S$  is added. There is no further precipitation. The precipitate is washed with water containing a little  $H_2S$  and some  $NH_4NO_3$ . The filtrate and washings are immediately concentrated by boiling to about 30 cc., and a yellow turbidity which results is removed by filtering through a double

filter and discarded. The precipitate of Group II is transferred to an evaporating dish. The precipitate is so small that we find it necessary to tear off the part of the paper not containing any precipitate and to remove the precipitate by placing the paper in an evaporating dish, adding a little water and stirring with a glass rod. The paper is finally removed.

An equal volume of  $\text{Na}_2\text{S}_x$  is added to the suspended precipitate. Since  $\text{Hg}^{++}$  is not present, we heat and stir with the glass rod. Most of the precipitate soon dissolves and a dark, gummy mass floats on the surface of the liquid. This we recognize as sulfur. We next dilute with about 10 cc. water, filter and wash with hot water. There is nothing to warrant the further analysis of the sulfur residue, so it is discarded. We have decided that subdivision A is not present. The  $\text{Na}_2\text{S}_x$  filtrate is now made just acid with  $\text{HCl}$  and heated and the yellow precipitate filtered and washed. The filtrate and washings are discarded. The precipitate is transferred to an evaporating dish and digested for fifteen minutes with concentrated  $(\text{NH}_4)_2\text{CO}_3$  solution and a piece of the solid reagent. We now dilute, filter and wash. The filtrate is made acid with  $\text{HCl}$ . No precipitate results, and neither is any obtained when  $\text{H}_2\text{S}$  is passed through. We conclude that arsenic is not present. The precipitate is now extracted four times with 12 cc. 12*n*  $\text{HCl}$ . There is a slight residue which we recognize to be sulfur. The filtrate, diluted to 65 cc. with water, is heated to boiling and  $\text{H}_2\text{S}$  is passed through for five minutes. As no precipitate results, we conclude that antimony is absent. Upon cooling, a yellow precipitate appears, which we conclude is  $\text{SnS}_2$ , indicating tin.

Returning to the filtrate from Group II, we first add 10 cc. 3*n*  $\text{NH}_4\text{Cl}$  and make alkaline with  $\text{NH}_4\text{OH}$ . No precipitate results. A side test with  $(\text{NH}_4)_2\text{S}$  shows Group III to be absent and the side-test solution is discarded.

We now pass directly to Group IV. We find that the concentration is right and that  $\text{NH}_4\text{Cl}$  has been added. A side test shows the presence of the group. We next add 10 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent. A white, finely divided suspension results. The solution is allowed to settle for an hour in a warm water bath and then the liquid is decanted through a filter paper. The precipitate which adheres to the bottom of the flask is washed once with cold water and the wash water is poured through the filter. The filtrate and washings

are reserved for Group V. The carbonate precipitate in the flask is dissolved in 10 cc. 6*n* acetic acid. A side test shows no  $\text{Ba}^{++}$  and the side test solution is discarded. The carbonates are not reprecipitated because there is no excess  $\text{K}_2\text{CrO}_4$  to remove. The solution is made alkaline with  $\text{NH}_4\text{OH}$  and a side test shows no  $\text{Sr}^{++}$  to be present. The side-test solution is added to the main solution.

The solution is now concentrated to 2 cc., cooled, made ammoniacal and 2 cc.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  reagent added. A white precipitate results and does not dissolve in concentrated  $\text{HAc}$ . We conclude  $\text{Ca}^{++}$  is present.

One-third of the filtrate for Group V is taken, and a few drops of  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  are added. The solution is concentrated to 3 cc., cooled and filtered through a double filter on account of a faint turbidity which appears. The clear filtrate is made ammoniacal and 2 cc.  $\text{Na}_2\text{HPO}_4$  added. As no precipitate results, even after standing, we conclude that  $\text{Mg}^{++}$  is absent.

We now take the two-thirds portion of the filtrate from Group IV and evaporate to dryness and after ignition take up with water and a few drops of  $\text{HCl}$ . Then 5 drops of  $\text{H}_2\text{PtCl}_6$  reagent are added. No precipitate results and we recall that there was no preliminary flame showing  $\text{K}^+$  so we conclude that the radical is absent.

Our final report shows that  $\text{Ag}^+$ ,  $\text{Sn}^{+4}$ ,  $\text{Ca}^{++}$  and  $\text{NH}_4^+$  are present.

## PART III

### THE NON-METALLIC RADICALS OR ANIONS

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#### CHAPTER I

#### SEPARATION OF ANIONS INTO GROUPS

**Preliminary Statement.**—The analysis of the non-metallic radicals, or anions, follows that of the cations principally because the general methods of procedure which must be used are a little more difficult for the beginner to handle. The more invariable any set of instructions can be made, the less skill is required of the person who is attempting to carry them out.

We have found in Part II that the cations can be analyzed in definite groups and that there is very little carrying over of radicals from one group to another. Very seldom was it suggested that special tests be made in the original solution. On the other hand, the tests were made to follow at definite places in carefully arranged procedures. Finally, it was suggested that after the solution had once been analyzed, confirmatory tests be made in the original solution by making the test in as few operations as possible and without repeating all of the steps as outlined in the systematic procedure. This short-cut method of making direct tests can only be used after an analysis of the sample has been completed.

It is evident that the direct test involves a better understanding of the reactions of the radicals than is required where all of the steps of a systematic procedure are followed. New combinations are likely to be of very frequent occurrence, and these require skill to handle.

In the analysis of a solution for acidic radicals, it is not the general custom to follow the group method, with the subsequent analysis by subdivision, as closely as with the basic constituents.

It must not be inferred that this is impossible to do, because a few schemes of analysis have been proposed in which this is accomplished with extreme detail; the reactions involved are chemically correct but time-consuming.

Where the metallic analysis has been completed, much information has been obtained which can be used in determining the non-metals. For example, when a clear, slightly acid solution has been analyzed and silver-ion identified, it will be found by referring to a table of solubilities that  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{AgSCN}$ ,  $\text{Ag}_3[\text{Fe}(\text{CN})_6]$ ,  $\text{Ag}_4[\text{Fe}(\text{CN})_6]$  and a few other compounds of silver can not be present. It is useless, therefore, to look for the corresponding acids. If your solution has been found to contain more than one metal, it follows that the possible presence of several acid radicals can be eliminated at once. Again, in the precipitation of the  $\text{H}_2\text{S}$  group, a change in color of the solution from yellow or orange to green will suggest the presence of chromates or dichromates, while the decolorizing of a reddish-purple solution will indicate the reduction of the permanganate ion. The presence of arsenites and arsenates will also be determined in metallic analysis.

**The Non-metallic Radicals.**—The list of acidic radicals included in our analytical work contains those which occur more commonly and whose identification is not too involved. The list includes the ions of the following:

Acetate, $\text{C}_2\text{H}_3\text{O}_2^-$	Nitrate, $\text{NO}_3^-$
Arsenate, $\text{AsO}_4^{-3}$	Nitrite, $\text{NO}_2^-$
Arsenite, $\text{AsO}_3^{-3}$	Oxalate, $\text{C}_2\text{O}_4^-$
Borates, $\text{BO}_3^{-3}$ , $\text{BO}_2^-$ , $\text{B}_4\text{O}_7^-$	Phosphate, $\text{PO}_4^{-3}$
Bromide, $\text{Br}^-$	Silicate, $\text{SiO}_3^-$
Carbonate, $\text{CO}_3^-$	Sulfate, $\text{SO}_4^-$
Chloride, $\text{Cl}^-$	Sulfide, $\text{S}^-$
Chromate, $\text{CrO}_4^-$ ; dichromate, $\text{Cr}_2\text{O}_7^-$	Sulfite, $\text{SO}_3^-$
Ferrieyanide $[\text{Fe}(\text{CN})_6]^{-3}$	Tartrate, $\text{C}_4\text{H}_4\text{O}_6^-$
Ferrocyanide $[\text{Fe}(\text{CN})_6]^{-4}$	Thiocyanate, $\text{SCN}^-$
Fluoride, $\text{F}^-$	Thiosulfate, $\text{S}_2\text{O}_3^-$
Iodide, $\text{I}^-$	

**Grouping the Anions.**—For convenience in analysis, the anions are arranged in groups, but it must be remembered that the groups are not consecutively separated by group precipitates and then



analyzed by subdividing, as with the cations. One of the common classifications is as follows:

Group I. The Volatile and Unstable Group.— $\text{CO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_3^-$ ,  $\text{S}^-$ ,  $\text{S}_2\text{O}_3^-$ ,  $\text{C}_2\text{H}_3\text{O}_2^-$ .

Group II. The Barium Chloride-Calcium Chloride Group.— $\text{AsO}_3^{-3}$ ,  $\text{AsO}_4^{-3}$ ,  $\text{BO}_3^{-3}$ ,  $\text{BO}_2^-$ ,  $\text{B}_4\text{O}_7^-$ ,  $\text{CrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^-$ ,  $\text{F}^-$ ,  $\text{C}_2\text{O}_4^-$ ,  $\text{PO}_4^{-3}$ ,  $\text{SiO}_3^-$ ,  $\text{SO}_4^-$ ,  $\text{C}_4\text{H}_4\text{O}_6^-$ .

Group III. The Silver Nitrate Group.— $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $[\text{Fe}(\text{CN})_6]^{-3}$ ,  $[\text{Fe}(\text{CN})_6]^{-4}$ ,  $\text{SCN}^-$ .

Group IV. The Soluble Group.— $\text{NO}_3^-$ .

## CHAPTER II

### GROUP I.—THE VOLATILE AND UNSTABLE GROUP <sup>1</sup>

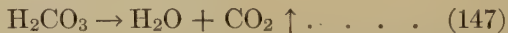
CARBONATE,	$\text{CO}_3^-$	SULFIDE,	$\text{S}^-$
NITRITE,	$\text{NO}_2^-$	THIOSULFATE,	$\text{S}_2\text{O}_3^-$
SULFITE,	$\text{SO}_3^-$	ACETATE,	$\text{C}_2\text{H}_3\text{O}_2^-$

This group of anions consists of acid radicals whose corresponding acids are readily volatilized by heating or are decomposed, and characteristic products are eliminated.

#### PRELIMINARY TESTS

##### CARBONATE-ION, $\text{CO}_3^-$ (COLORLESS)

**1. Carbonic Acid,  $\text{H}_2\text{CO}_3$ .**—Add, dropwise, 2 cc. 3*n* HCl to 2 cc. test solution of  $\text{Na}_2\text{CO}_3$ . The active bubbling of gas in a liquid is **effervescence**. The equations are:



Does the HCl react only with  $\text{Na}_2\text{CO}_3$  (recall hydrolysis)? Write a second set of equations for this possibility. Is carbonic acid actually given off? Is all of the  $\text{CO}_2$  eliminated without heating the solution? Does the acid exist outside of a solution? Add, to another portion of  $\text{Na}_2\text{CO}_3$  solution, a few drops of  $\text{H}_2\text{SO}_4$ . Result? Do the same with acetic acid. Does it appear that  $\text{CO}_2$  can be eliminated from  $\text{Na}_2\text{CO}_3$  in any acid solution?

**2. Carbonates of the Alkaline-earth Metals.**<sup>2</sup>—We have used

<sup>1</sup> Tradition seems to have established the cyanide radical CN in this group together with voluminous notes explaining why it should be omitted from laboratory practice. It will be omitted in this text without further comment.

<sup>2</sup> The object of this type of paragraph heading is to correlate the tests made with non-metals with tests involving metallic radicals. In this so-called lime-water test there is nothing new presented in addition to that covered in the alkaline-earth group. The method of applying the test requires further consideration, however.

insoluble carbonates in the identification of the alkaline-earth metals; why not use the same precipitates to identify the  $\text{CO}_3^{=}$  radical?

Make a saturated solution of  $\text{Ca}(\text{OH})_2$  (lime water) by filling a test tube one-fifth full of  $\text{Ca}(\text{OH})_2$  powder and then adding water until two-thirds full. Now thoroughly shape the contents of the tube and slowly boil for about five minutes. Loosely insert a cork stopper in the test tube and set aside to settle. Label this

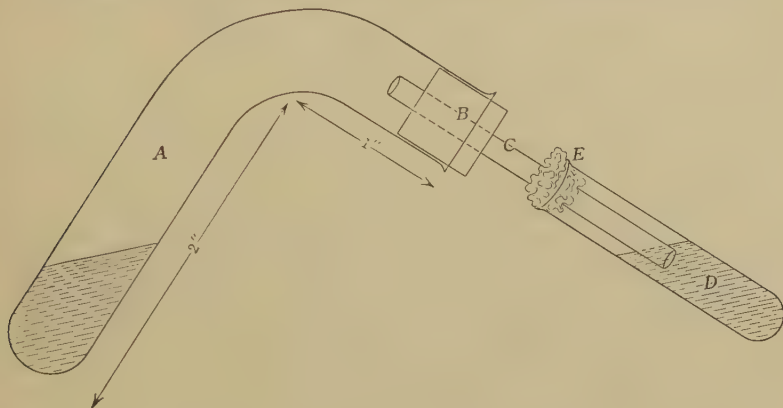


FIG. 11.—Small Bent-tube Distilling Apparatus.

In the separation and identification of several anions it is necessary to make distillations with small amounts of substances. Unless the apparatus used is small and gas-tight satisfactory results will not be obtained. Take a 3-inch test tube and bend at about 1 inch from the open end so that an angle of approximately  $90^\circ$  is formed by the two arms. The tube will flatten slightly at the bend but this is an advantage. Fit a one-hole rubber stopper *B*, through which passes a piece of glass tubing *C* about 2 inches long. The lower end of the tubing is placed just under the liquid in *D* which is used to collect the distillate. Very little back pressure will be caused by this arrangement. The collecting tube *D* can be stoppered loosely with a plug of cotton *E* to prevent the escape of gases.

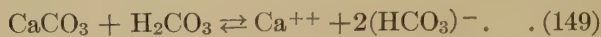
This apparatus is not only small and gas-tight but has the additional advantage of preventing any liquid that may be drawn back through the tube *C* from becoming mixed with the substance in *A*. When any liquid is drawn back it will remain in the right arm of the large tube just back of the stopper.

reagent and keep it in your desk. Do not remove the sediment. Carefully decant some of the supernatant liquid when you are to make lime-water tests. Solutions of  $\text{Ca}(\text{OH})_2$  not in equilibrium with the solid are soon exhausted in contact with air. Explain. Is the solution concentrated? Is it saturated?

A similar solution made with  $\text{Ba}(\text{OH})_2$  is stronger. Why? What is a common name for this solution? You are asked to keep the lime-water reagent in your desk because it is worthless unless

saturated and perfectly clear. A solution of lime water in a stock bottle sometimes becomes exhausted, and, furthermore, students may disturb the solution and make it turbid.

Make a distilling tube as shown in Fig. 11. Add 1 cc. test solution of  $\text{Na}_2\text{CO}_3$  to the distilling tube, dilute with 2 cc. water, then add 2 cc.  $3n$   $\text{HCl}$ . Distill into 2 cc. lime water. Continue the distillation until a good precipitate of  $\text{CaCO}_3$  has been formed and then is redissolved. The reactions are:



Take the clear solution of calcium bicarbonate and boil. What is the result? Write the equation. In making this test for a carbonate, what precaution must be observed?

The lime-water test is sometimes made by taking a platinum wire looped at the end, such as you used in the bead tests. By dipping in lime water, a film will be contained in the loop. By carefully holding this film in the vapors coming from the decomposition of a carbonate solution, the opaqueness due to the formation of  $\text{CaCO}_3$  can be obtained. Two drawbacks to this film method of testing consist of the ease with which the film is broken by the liquid in the tube spattering on account of effervescence or boiling, and the quickness with which the film may cloud up and become transparent again. To avoid these difficulties, the loop should be held about 1 inch above the liquid being tested and then withdrawn every few seconds for observation.

**3. Additional Precipitate of Carbonate-ion.**—Silver carbonate,  $\text{Ag}_2\text{CO}_3$ , white, and slightly decomposed into  $\text{Ag}_2\text{O}$  by boiling. The resulting mixture of  $\text{Ag}_2\text{CO}_3$  and  $\text{Ag}_2\text{O}$  is yellow or a yellowish-brown.

### EXERCISES

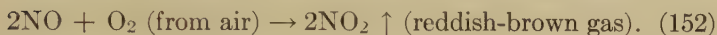
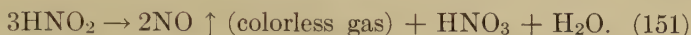
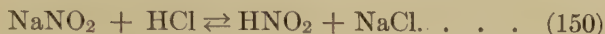
1. Make a list of the names that have been applied to  $\text{CO}_2$ . There are at least three.
2. How do you know that there is an acid,  $\text{H}_2\text{CO}_3$ ?
3. Can carbonic acid be liquefied?
4. Is it proper to conclude that carbonic acid is weaker than acetic acid because it can be eliminated from a solution containing acetic acid? Write all the equilibria necessary to give a complete discussion.
5. In the precipitation of  $\text{CaCO}_3$  in metallic analysis, which ion was

present in limited amount? Which in excess? Are the conditions any different in this non-metal test?

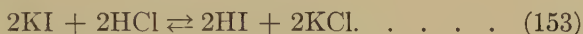
6. Lime-water has been the most commonly used hydroxide in testing for  $\text{CO}_2$ . Is there any objection to the use of solutions of  $\text{Sr}(\text{OH})_2$  or  $\text{Ba}(\text{OH})_2$ ?

### NITRITE-ION, $\text{NO}_2^-$ (COLORLESS)

1. **Nitrous Acid,  $\text{HNO}_2$ .**—Add, dropwise, 2 cc. 3*n* HCl to 2 cc. test solution of  $\text{NaNO}_2$ . Warm if necessary to expel the NO gas which changes to brown  $\text{NO}_2$  in contact with the air. The reactions are:



Since there may be other colored gases evolved, there must be a further identification for  $\text{NO}_2$ . One test involves holding a moist piece of KI-starch paper in the vapors coming from the tube. This paper consists of strips of filter paper moistened with a drop of KI solution and another drop of boiled starch suspension.<sup>3</sup> The reactions are:



The blue color on the starch is caused by the finely dispersed particles of iodine held on the gelatinous surface of the starch. There is no chemical reaction between the starch and the iodine.

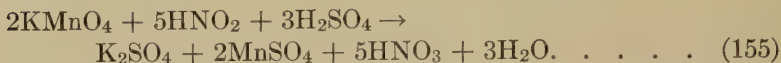
2. **Ferrous-nitrosyl Sulfate,  $\text{Fe} \cdot \text{NO} \cdot \text{SO}_4$ .**—Acidify a test solution of a nitrite with 6*n*  $\text{H}_2\text{SO}_4$ . Now add 5 drops freshly prepared  $\text{FeSO}_4$  solution or a solution of ferrous ammonium sulfate. Place in a test tube and hold in an inclined position. Slowly run down the inside of the tube about 2 cc. concentrated  $\text{H}_2\text{SO}_4$ . There should be two distinct liquid layers forming a brown ring at the junction and consisting of  $\text{Fe} \cdot \text{NO} \cdot \text{SO}_4$  (see Plate V, B and C).

<sup>3</sup> Boiled starch suspension is prepared just before use by taking about 0.1 gram of any starch, adding a few drops of water and rubbing into a cream. Now dilute with 10 cc. of water and carefully bring to a boil. The suspension can be kept for some time by adding a preservative, but care must be taken that the substances added will not interfere with subsequent tests. Avoid the use of so-called soluble starches because the starch granules must be burst by boiling and not dextrinized as in soluble starches. It is the sticky gelatinous surface that is required to adsorb the iodine suspension.



By referring to equation (151) it will be seen that in an acid solution of a nitrite, there is formed  $\text{HNO}_3$  as well as  $\text{HNO}_2$ . The ring test just given is a direct test for a nitrate.

**3. Reducing Action of  $\text{HNO}_2$ .**—In the KI-starch test, nitrous acid reacts as an oxidizing agent, but it can also reduce, as shown by the following:



What indication do you have that the permanganate has been reduced?

**4. Ammonium Nitrite,  $\text{NH}_4\text{NO}_2$ .**—The nitrite radical can be eliminated by forming a solution of  $\text{NH}_4\text{NO}_2$  and then boiling. To show this reaction, take 1 cc.  $\text{NaNO}_2$  solution, dilute in a test tube with 5 cc. water and add 1 gram of solid  $(\text{NH}_4)_2\text{SO}_4$ . Clamp the test tube in a slanting position and boil slowly for fifteen minutes. Take 1 cc. of this solution and test for a nitrite; if still present, add more  $(\text{NH}_4)_2\text{SO}_4$  and water and boil for another period. The equations are:



**5. Test with Sulfanilic Acid—Naphthylamine.**—Since nitrites are very difficult to test for in the presence of nitrates, special reagents have been prepared to make the identification. Take 5 cc. of a 0.001*n* solution of  $\text{NaNO}_2$  and add a few drops of the special solution of sulphanilic acid—naphthylamine and warm. A pink color is a specific test for a nitrite.

**6. Additional Precipitates of the Nitrite-ion.**— $\text{AgNO}_2$ , white;  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ , yellow.

### EXERCISES

1. If nitrous acid cannot be separated from a solution, what evidence is there that the acid exists? Are nitrite salts stable?
2. Explain the electron transfer involved in the KI-starch paper test for a nitrite.
3. What would be the effect of using a KBr-starch paper for a nitrite test?
4. Show the electron transfer in the reaction between nitrous acid and a permanganate.
5. Suggest another method for showing the presence of free iodine besides adsorbing it on starch granules.

SULFITE-ION,  $\text{SO}_3^-$  (COLORLESS)

**1. Sulfurous Acid,  $\text{H}_2\text{SO}_3$ .**—Add 2 cc. 3*n* HCl to 2 cc. test solution of  $\text{Na}_2\text{SO}_3$ . Warm if bubbles of gas do not form readily. The reactions are:



Under what conditions will these two reactions run to completion? How could you have them come to equilibrium?

**2. Sulfitcs of the Alkaline-earth Metals.**—Place 2 cc.  $\text{Na}_2\text{SO}_3$  test solution in the small distilling tube, add 1 cc. water and 2 cc. 6*n* HCl. Distill the  $\text{SO}_2$  into 2 cc. test solution of  $\text{Sr}(\text{NO}_3)_2$ . Describe the precipitate and write the equation. Does the precipitate dissolve in an excess of  $\text{SO}_2$ ? Distill  $\text{SO}_2$  into test solutions of  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Ca}(\text{NO}_3)_2$ . Compare the last three results.

Now distill  $\text{SO}_2$  into solutions of  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$ . Is a precipitate formed in each case? Is there any difference in the formation of the sulfites from a solution of a nitrate and a solution of an hydroxide? Which solution is best to use in testing for the presence of  $\text{SO}_2$ ?

Since there is a white precipitate formed in  $\text{Sr}(\text{NO}_3)_2$  solution by both  $\text{CO}_2$  and  $\text{SO}_2$ , we must remove one or the other if both are present in a solution and this test is to be used. The carbonate cannot be removed without the consequent removal of the sulfite, but it is possible to change the sulfite to a sulfate without destroying the carbonate. Add 1 cc.  $\text{K}_2\text{Cr}_2\text{O}_7$  reagent to another 2 cc. portion of  $\text{Na}_2\text{SO}_3$  in the distilling tube. Add 2 cc. 6*n* HCl and shake several times. Warm gently before distilling into the  $\text{Sr}(\text{NO}_3)_2$  solution. You can judge from the results how thoroughly the sulfite is changed to the stable sulfate, and revise the time for oxidation if necessary. It is evident that, since both  $\text{SO}_2$  and  $\text{CO}_2$  when passed into a solution of  $\text{Sr}(\text{NO}_3)_2$ , form the two white precipitates of  $\text{SrSO}_3$  and  $\text{SrCO}_3$ , the sulfite must be perfectly removed in order to obtain a satisfactory test for the carbonate.

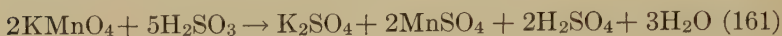
The sulfite of barium, but not that of calcium, is precipitated in a manner similar to that of strontium sulfite.

**3. Reducing Action of  $\text{H}_2\text{SO}_3$ .**—Iodine solutions are bleached by sulfurous acid according to:



How can the reducing action be followed?

A permanganate solution in an excess of sulfuric acid is bleached by sulfurous acid:



A dichromate can also be reduced as shown by:



**4. Additional Precipitate of Sulfite-ion.**—Silver sulfite,  $\text{Ag}_2\text{SO}_3$ , white.

### EXERCISES

1. Show the electron transfer in the equations given in Section 3.
2. Write an equation and show the electron transfer when  $\text{H}_2\text{SO}_3$  reduces  $\text{FeCl}_3$  to  $\text{FeCl}_2$ .
3. Try to determine what will be the result of bringing  $\text{SnCl}_2$  and  $\text{H}_2\text{SO}_3$  together.

### SULFIDE-ION, $\text{S}^\circ$ (COLORLESS)

**1. Hydrosulfuric Acid,  $\text{H}_2\text{S}$ .**—Add 2 cc. 3*n* HCl to 2 cc. test solution of  $\text{Na}_2\text{S}$ . This is the first member of Group I that has been volatilized without decomposition. Write the reaction. Where the acidity is high or oxidizing agents are present, quite a part of the  $\text{H}_2\text{S}$  will be decomposed and  $\text{S}^\circ$  eliminated. What becomes of the  $2\text{H}^+$ ?

It might seem that a gas with such a characteristic odor as  $\text{H}_2\text{S}$  could be identified anywhere, but if the amount is relatively small and there is also  $\text{SO}_2$  or other pungent gases coming off, a more certain method is necessary.

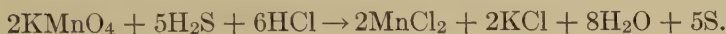
Take a strip of filter paper, moisten one end with 2 drops of lead acetate solution and test for the gas as you did in metallic analysis when it was desired to determine that an excess of  $(\text{NH}_4)_2\text{S}$  reagent was present. (Refer to Group III of metals.)

**2. The Reducing Action of  $\text{H}_2\text{S}$ .**—The reducing action of  $\text{H}_2\text{S}$  has received special consideration in Group II of metals. With a dichromate the reaction is shown by:



What is the change of color in this reduction process?

The bleaching of potassium permanganate is shown by:



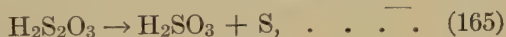
**3. Additional Precipitates of Sulfide-ion.**—Silver sulfide,  $\text{Ag}_2\text{S}$ , black; also sulfides of other members of Groups I, II and III of metals.

### EXERCISES

1. Write the equations for the reaction of  $\text{H}_2\text{S}$  with (a) iodine; (b) sulfurous acid; (c) nitric acid; (d) ferric chloride.
2. What will be the effect of  $\text{H}_2\text{S}$  on KI-starch paper?
3. How many solutions have we found so far that will act as bleaching agents?
4. Why is  $\text{H}_2\text{S}$  named hydrosulfuric acid?

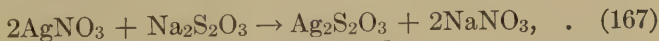
THIOSULFATE-ION,  $\text{S}_2\text{O}_3^{=}$  (COLORLESS)

**1. Thiosulfuric Acid,  $\text{H}_2\text{S}_2\text{O}_3$ .**—Take 2 cc. test solution of  $\text{Na}_2\text{S}_2\text{O}_3$  and dilute with 5 cc. water. Add, dropwise,  $3n$   $\text{HCl}$  until acid, then 1 cc. in excess. The reactions are:



What combination of acids also yields  $\text{SO}_2$  and  $\text{S}$  upon decomposing?

**2. Silver Thiosulfate,  $\text{Ag}_2\text{S}_2\text{O}_3$ .**—Take 3 cc. test solution of  $\text{AgNO}_3$  and add, dropwise, a solution of  $\text{Na}_2\text{S}_2\text{O}_3$ . After a white precipitate has been formed continue the addition until the precipitate is entirely dissolved. The reactions are:



What type of salt has been formed?

Boil the solution obtained above. Describe the color changes. The final product is black  $\text{Ag}_2\text{S}$ .

**3. The Reducing Action of  $\text{H}_2\text{S}_2\text{O}_3$ .**—The reducing action is that of  $\text{SO}_2$ , one of its decomposition products (refer to sulfites).

### EXERCISES

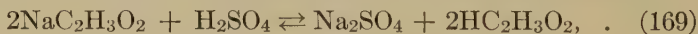
1. Write the structural formula for  $\text{H}_2\text{S}_2\text{O}_3$ .
2. What is the common name for  $\text{Na}_2\text{S}_2\text{O}_3$ ? Explain how it dissolves the halides of silver.
3. Write an equation to show the reaction between  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{I}_2$ .
4. How will a solution of  $\text{Na}_2\text{S}_2\text{O}_3$  react toward litmus? Give a full explanation. Is a thiosulfate of a weak metallic radical possible? What about  $\text{Ag}_2\text{S}_2\text{O}_3$ ?

ACETATE-ION,  $\text{C}_2\text{H}_3\text{O}_2^-$ , (COLORLESS)

**1. Acetic Acid,  $\text{HC}_2\text{H}_3\text{O}_2$  or  $\text{CH}_3\text{COOH}$ .**—The  $\text{O}=\overset{\textstyle |}{\text{C}}-\text{OH}$  group is a characteristic organic acid group and the hydrogen which it contains is replaceable.

Add 3 cc.  $3n$   $\text{HCl}$  to 3 cc. test solution of  $\text{NaAc}$  and warm. Describe the characteristic odor of acetic acid. Use  $6n$   $\text{H}_2\text{SO}_4$  in place of the  $3n$   $\text{HCl}$ . Is the odor of the acid any stronger? Explain.

Add 2 cc. of 95 per cent ethyl alcohol to 3 cc. test solution of  $\text{NaAc}$  and then add, dropwise, 2 cc.  $12n$   $\text{H}_2\text{SO}_4$ . Warm and compare the odor with that of alcohol alone. The reactions are:



The compound  $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$  is ethyl acetate and is typical of a class of organic salts known as **esters**. What is the name of the reverse reaction in the second equation? Will the formation of the ester take place better in a dilute or a concentrated solution? Give reason for your answer.

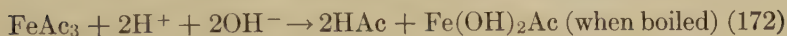
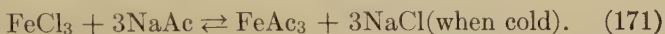
In making a test for an ester it is necessary to have another tube with alcohol alone, for comparison. There is always some alcohol which comes off with the ester and you may associate the alcohol odor with that of the ester.

A more characteristic ester is that obtained when amyl alcohol is used in place of the ethyl alcohol. Prepare this ester.

**2. Basic Acetates.**—Place 2 cc. test solution of  $\text{FeCl}_3$  in a test tube, add 5 cc. water and carefully neutralize with  $\text{NH}_4\text{OH}$  until



there is a very slight precipitate of  $\text{Fe}(\text{OH})_3$  formed. If you exceed this amount of precipitate add  $\text{HAc}$  until the precipitate has just about redissolved. Now add 5 cc. of a solution of  $\text{NH}_4\text{Ac}$  or  $\text{NaAc}$  and boil. Describe the color of the solution and the formation of the precipitate. The reactions are:



Test the solubility of some of the basic ferric acetate in  $6N$   $\text{HCl}$ . Under what conditions of acidity will basic acetates be precipitated?

The basic acetate of aluminum is formed in a manner similar to that of iron. An analogous compound of chromium is more soluble and frequently very irregular in precipitating.

**3. Decomposition of Acetates.**—Heat some  $\text{NaAc}$  on a porcelain crucible cover. The reaction is:



The compound  $(\text{CH}_3)_2\text{CO}$  is acetone. When alkaline earth acetates are heated, the oxide of the metal results. Note that acetates, although of organic origin, like oxalic acid, do not char by heating.

### EXERCISES

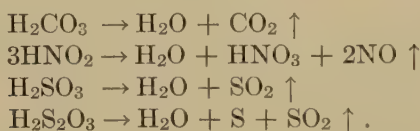
1. The formula for amyl alcohol is  $\text{C}_5\text{H}_{11}\text{OH}$ . Write the equation for the reaction with acetic acid.
2. For what purposes is the concentrated  $\text{H}_2\text{SO}_4$  used in the preparation of an ester? In what respects is it better than  $\text{HCl}$ ?
3. Show by equilibrium reactions how increased acidity will decrease the  $\text{Ac}^-$  ion which is necessary for the formation of  $\text{FeAc}_3$ .
4. Explain the effect of increased acidity upon the hydrolysis of  $\text{FeAc}_3$ .
5. What are the possible reactions in a solution containing  $\text{FeCl}_3$  and  $\text{NaAc}$ ? State your own conditions of acidity.

### SUMMARY OF REACTIONS OF THE ACIDS AND ACID-IONS IN THE VOLATILE AND UNSTABLE GROUP THAT ARE OF IMPORTANCE IN ANALYTICAL PROCEDURE

We have seen that when acids are added to soluble salts of members of this group the free acids are formed by double decomposition. These may be volatilized by heating or may break up into characteristic products which in turn are eliminated by heat.

Hydrosulfuric and acetic acids are evolved with little decomposition, and  $\text{H}_2\text{S}$  can be identified by means of filter paper moistened with lead acetate or any soluble salt whose sulfide is a colored precipitate. The identification of acetic acid is usually made by means of the characteristic odor of ethyl or amyl esters. Although acetates are organic compounds they do not char by heating.

The remaining acids of the group give characteristic decomposition products when heated, and their identification resolves itself into an identification of one of the products. The following list shows the decomposition products, and the characteristic gas which is evolved is placed last:



In testing for  $\text{CO}_2$  we have found that the formation of the alkaline earth carbonates is satisfactory provided sulfites and thiosulfates are absent. This conflict can be eliminated by adding an oxidizing agent before heating because  $\text{SO}_3^-$  will be oxidized to  $\text{SO}_4^-$  which does not decompose, and the  $\text{CO}_3^-$  will remain unchanged.

In the identification of  $\text{NO}$  we can make use of the formation of the brown gas  $\text{NO}_2$  as long as we are confined to this group, but later, when we are dealing with other colored gases that may be evolved, this test must be modified. The oxidizing action of  $\text{HNO}_2$  upon KI-starch paper is a satisfactory test, provided strong reducing agents, which may also be present, do not interfere. The reducing action of  $\text{KNO}_2$  is not a useful test because, as we have seen,  $\text{H}_2\text{S}$  and  $\text{SO}_2$  can also reduce. The elimination of a nitrite from a solution can be accomplished by converting it into  $\text{NH}_4\text{NO}_2$  and heating. Special reagents have been prepared for identifying a nitrite. These are of value where a nitrate also is present.

As a test for  $\text{SO}_2$  in the presence of  $\text{CO}_2$ , we have found that the formation of alkaline-earth metal sulfites is not conclusive, although  $\text{CaSO}_3$  is much more soluble than  $\text{CaCO}_3$ . The odor of  $\text{SO}_2$  is characteristic although it may be obscured in the presence of other pungent gases. The bleaching or reducing action of  $\text{SO}_2$  is useful where  $\text{HNO}_2$  and  $\text{H}_2\text{S}$  have been found to be absent. Since  $\text{SO}_2$  may result from  $\text{H}_2\text{SO}_3$  or  $\text{H}_2\text{S}_2\text{O}_3$ , it is necessary to remember that

in the decomposition of the latter, S also results. The amount of S that may result from the decomposition of  $\text{H}_2\text{S}$  is usually very small in comparison with that from a thiosulfate.

The precipitates of the acids of this group with  $\text{AgNO}_3$  are worth taking into consideration. Although the precipitates  $\text{Ag}_2\text{CO}_3$ ,  $\text{AgNO}_2$  and  $\text{Ag}_2\text{SO}_3$  are white, that of  $\text{Ag}_2\text{CO}_3$  will change to yellow or brown when heated. The precipitate of  $\text{Ag}_2\text{S}$  is black and that of  $\text{Ag}_2\text{S}_2\text{O}_3$  is white but redissolves in excess of  $\text{H}_2\text{S}_2\text{O}_3$ .

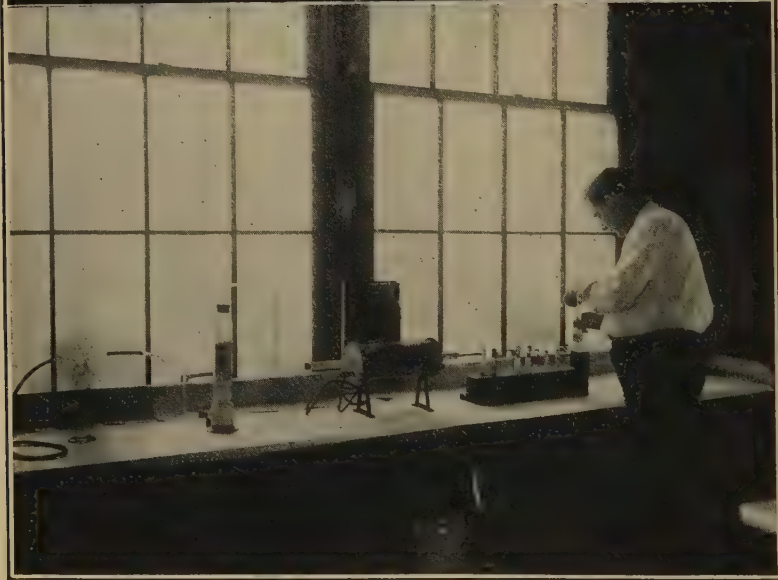
#### PROCEDURE FOR THE ANALYSIS OF A PRACTICE SOLUTION CONTAINING ACID RADICALS OF GROUP I, THE VOLATILE AND UNSTABLE GROUP

Take one-half of the sample, as usual, for immediate analysis.

**Preliminary Test.**—A preliminary examination will be made with  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  by placing 3 cc. of the solution in a 3-inch test tube and then adding 2 cc. of  $3n$   $\text{HCl}$ , the first portion dropwise. Carefully note an active evolution of gas which usually indicates a carbonate, in contrast with the slower decomposition of a nitrite. Warm gently and determine the color and odor of gases evolved. Also make tests, as the decomposition progresses, with KI-starch paper and  $\text{Ba}(\text{OH})_2$  solution in a platinum-wire loop. See if any S is deposited in the solution or on the sides of the tube. Now add a few drops of  $12n$   $\text{H}_2\text{SO}_4$  and, after noting results, warm gently. By this gradual decomposition action of  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ , it is often possible to have the gases evolved in stages so that the individual characteristics can be determined better.

**Identification of Carbonates.**—To confirm the preliminary tests already obtained, place 3 cc. of the solution in the small bent distilling tube, add 2 cc.  $\text{K}_2\text{Cr}_2\text{O}_7$ , reagent,<sup>a</sup> shake several times and warm gently. Add 3 drops  $3n$   $\text{HCl}$  and after five minutes add 2 cc. more of the acid and distill into a saturated solution of  $\text{Ca}(\text{OH})_2$ .<sup>b</sup> A white precipitate of  $\text{CaCO}_3$  indicates a carbonate.

**Identification of Nitrites.**—The evolution of a brown gas when we are restricted to this group indicates  $\text{NO}_2$  from a nitrite. The KI-starch paper test can be repeated if there was not sufficient time in the preliminary test to obtain satisfactory results. Use for this purpose 2 cc. of the solution, and 2 cc.  $3n$   $\text{HCl}$  and warm, adding a few drops of  $12n$   $\text{H}_2\text{SO}_4$  if necessary.



Many qualitative tests are later used in quantitative determinations.

*Above.*—The end-point in this determination is shown by the formation of the red molecules of  $\text{Fe}(\text{SCN})_3$ .

*Below.*—The determination of carbon is not made with a very high degree of accuracy in elementary qualitative analysis. This photograph shows a "combustion train" in which the resulting  $\text{CO}_2$  is quantitatively determined.



**Identification of Sulfites.**—The characteristic odor of  $\text{SO}_2$  in the preliminary test may have been very prominent. To confirm further in the absence of carbonate, use the  $\text{BaSO}_3$  test. For your distilling mixture take 2 cc. of the solution, and 2 cc.  $3n$   $\text{HCl}$  and distill into 3 cc. of a saturated solution of  $\text{Ba}(\text{OH})_2$ . A white precipitate of  $\text{BaSO}_3$  indicates a sulfite. Where carbonates are present, distill as outlined above into 1 cc. of a permanganate solution which is so dilute that it has only a faint pink color. The decolorizing of the solution will indicate a sulfite, provided a nitrite, sulfide or thiosulfate is not present. There are tests for the three latter radicals that do not involve bleaching<sup>c</sup>.

**Identification of Sulfides.**—If the preliminary test with lead acetate paper was not conclusive, place 1 cc. of the solution in a small test tube, add 1 cc.  $6n$   $\text{HCl}$ <sup>d</sup> and a few drops  $12n$   $\text{H}_2\text{SO}_4$  and warm. The formation of black  $\text{PbS}$  on the  $\text{PbAc}_2$  test paper confirms a sulfide.

**Identification of Thiosulfates.**—Take 2 cc. of the solution and add, dropwise,  $3n$   $\text{HCl}$  until acid. There is usually an abundant precipitate of  $\text{S}$  if a thiosulfate is present. Warm and add a few more drops of acid if only a turbidity results. Identify  $\text{SO}_2$  as you did in the case of a sulfite if it cannot be identified otherwise. The presence of  $\text{SO}_2$  and  $\text{S}$  confirms a thiosulfate<sup>e</sup>.

It was pointed out in the section on thiosulfates that the reaction between  $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{S}$  liberates  $\text{S}$ , hence it is evident that the tests given thus far cannot be used for the detection of a thiosulfate in the presence of a sulfite and a sulfide. There are procedures to handle this difficult situation but they are quite involved.

**Identification of Acetates.**—If the odor of acetic acid is not conclusive, make a test with an ester by taking 2 cc. of the solution, adding 1 cc. amyl alcohol and then 5 drops  $12n$   $\text{H}_2\text{SO}_4$ . Warm gently<sup>f</sup> and compare with the odor of amyl alcohol. The characteristic **amyl acetate** confirms the presence of an acetate.

#### NOTES ON THE PROCEDURE FOR THE ANALYSIS OF A PRACTICE SOLUTION CONTAINING GROUP I ANIONS

a. The test for  $\text{CO}_2$  is made before that for  $\text{SO}_2$  because a precipitate of  $\text{BaCO}_3$  showing the presence of  $\text{CO}_2$  can be obtained to the exclusion of  $\text{BaSO}_3$ . If it is found that carbonates are absent, then by repeating this test in the absence of  $\text{K}_2\text{Cr}_2\text{O}_7$ , a white precipitate will confirm  $\text{SO}_2$ . It is necessary to confirm  $\text{SO}_2$  where a thiosulfate is present also.



b. Your preliminary test with  $K_2Cr_2O_7$ , where a sulfite was oxidized to a sulfate, was outlined in great detail. You should be absolutely certain by this time under what conditions complete oxidation of the sulfite will take place.

c. It is evident that the presence of a sulfite will not make it impossible to obtain positive tests for a carbonate, nitrite, sulfide and thiosulfate, but the reverse is not true. A special regrouping of radicals is necessary in a situation of this sort, and this will be considered in the complete analysis of solutions.

d. Certain solid sulfides are not decomposed by this acid treatment but, since we are analyzing a solution, this consideration will be reserved to the appropriate chapter that deals with the analysis of solids.

e. Although  $H_2S$  in a strong acid solution, and especially upon boiling, will liberate S, there should not be any confusion with a thiosulfate where the acidity is gradually increased as just outlined. The S from a thiosulfate usually appears just as soon as the solution is made acid and even before there is an evolution of  $SO_2$ .

f. Alcohols will burn. Use care in warming. If alcohol takes fire, smother the flame with a wet towel or sand. Never throw the solution out of the container.

## CHAPTER III

### GROUP II.—THE BARIUM CHLORIDE- CALCIUM CHLORIDE GROUP

ARSENITE,	$\text{AsO}_3^{-3}$	OXALATE,	$\text{C}_2\text{O}_4^{-}$
ARSENATE,	$\text{AsO}_4^{-3}$	PHOSPHATE,	$\text{PO}_4^{-3}$
BORATE,	$\text{BO}_3^{-3}$ , $\text{BO}_2^{-}$ , $\text{B}_4\text{O}_7^{-}$	SILICATE,	$\text{SiO}_3^{-}$
CHROMATE,	$\text{CrO}_4^{-}$ , $\text{Cr}_2\text{O}_7^{-}$	SULFATE,	$\text{SO}_4^{-}$
FLUORIDE,	$\text{F}^{-}$	TARTRATE,	$\text{C}_4\text{H}_4\text{O}_6^{-}$

This group of anions is characterized, in the absence of Group I, by forming precipitates with the  $\text{BaCl}_2$ - $\text{CaCl}_2$  reagent in a neutral or slightly alkaline solution.

#### PRELIMINARY TESTS

#### CONDITIONS WHICH MUST BE PRESENT WHEN THE $\text{BaCl}_2$ - $\text{CaCl}_2$ GROUP IS PRECIPITATED

To show the general reacting characteristics of the group, take 5 cc. test solution of  $\text{Na}_2\text{HPO}_4$ , add 10 drops of 6*n* HCl and 7 cc. water. Divide into 6 parts in the same number of test tubes. Add to the first test tube 1 cc. of a test solution of  $\text{AgNO}_3$ ; to the second, 1 cc. of  $\text{CuSO}_4$ ; to the third, 1 cc. of  $\text{FeCl}_3$ ; to the fourth, 1 cc. of  $\text{BaCl}_2$ ; to the fifth, 1 cc. of  $\text{MgCl}_2$ ; and to the sixth, 1 cc. of KCl. Now make each of the six solutions alkaline with  $\text{NH}_4\text{OH}$ . What you have just determined with the phosphate is quite generally true of the entire group. By referring to the solubility tables it will be found that in an alkaline solution all of the metallic radicals, with the exception of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ , will be precipitated by a majority of the acid radicals in this group. It, therefore, follows that if Group II of acid radicals is to be precipitated by the  $\text{BaCl}_2$ - $\text{CaCl}_2$  reagent, the metallic radicals, with the exception of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ , must be absent.

In the preliminary tests involving this group we shall use solutions of sodium salts, and later in the complete analysis of a

solution it will be necessary to make a special solution which will be designated as a **Prepared Solution** in order to eliminate the conflicting metallic radicals before Group II is precipitated.

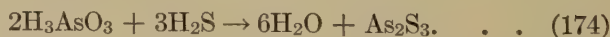
There is another preliminary requirement to be fulfilled. We have found that  $\text{BaCO}_3$  and  $\text{BaSO}_3$  are precipitated in a solution that is not acid. What other acid radicals of Group I will form precipitates with the  $\text{BaCl}_2$ - $\text{CaCl}_2$  reagent? The second requirement is, therefore, to have the volatile group eliminated before Group II is precipitated.

The reagent  $\text{BaCl}_2$ - $\text{CaCl}_2$  is used, and not  $\text{BaCl}_2$  or  $\text{CaCl}_2$  alone, because, as we have noticed in the study of the alkaline-earth group, the maximum insolubility of compounds involving radicals of this metallic group contained the  $\text{Ba}^{++}$  ion in some cases and the  $\text{Ca}^{++}$  ion in others. Another explanation would be that the solubility increased from Ba to Ca in one series and from Ca to Ba in another series. By combining  $\text{BaCl}_2$  and  $\text{CaCl}_2$ , the maximum precipitating action of the alkaline-earth group radicals is obtained.

#### ARSENITE-ION, $\text{AsO}_3^{-3}$ (COLORLESS)

**1. Barium Arsenite,  $\text{Ba}_3(\text{AsO}_3)_2$ , and Calcium Arsenite,  $\text{Ca}_3(\text{AsO}_3)_2$ .**—Add an excess of a  $\text{BaCl}_2$  solution to 3 cc. test solution of  $\text{Na}_3\text{AsO}_3$ . Repeat the experiment, using  $\text{CaCl}_2$ . Describe the two precipitates and determine which of the two precipitating reagents is the more efficient. How does a solution of  $\text{Na}_3\text{AsO}_3$  react toward litmus? Test the solubility of the precipitate in  $6n$   $\text{HCl}$  and  $6n$   $\text{HNO}_3$ .

**2. Arsenious Acid,  $\text{H}_3\text{AsO}_3$ .**—Add 1 cc.  $3n$   $\text{HCl}$  to 3 cc. test solution of  $\text{Na}_3\text{AsO}_3$ . Write the equation. Is arsenious acid very stable? Pass  $\text{H}_2\text{S}$  slowly through the solution. Does the precipitate form instantly? Compare later with a similar test involving arsenic acid. The reaction is:



How was the formation of a sulfosalt prevented in precipitating the  $\text{H}_2\text{S}$  group?

**3. Silver Arsenite,  $\text{Ag}_3\text{AsO}_3$ .**—Take 2 cc. test solution of  $\text{Na}_3\text{AsO}_3$  and precipitate with a solution of  $\text{AgNO}_3$  reagent. Adjust the solution containing the precipitate so that it is nearly

neutral. Will neutral solutions of  $\text{AgNO}_3$  and of  $\text{Na}_3\text{AsO}_3$  necessarily give a neutral solution of  $\text{Ag}_3\text{AsO}_3$ ? Test the solubility of this precipitate in  $12n$   $\text{HNO}_3$  and in  $6n$   $\text{NH}_4\text{OH}$ .

**4. Magnesium Ammonium Arsenite,  $\text{MgNH}_4\text{AsO}_3$ .**—Add to 3 cc. test solution of  $\text{Na}_3\text{AsO}_3$  first 1 cc.  $3n$   $\text{NH}_4\text{OH}$ , then 2 cc. of a test solution of  $\text{MgCl}_2$ . No precipitate should form, but if there is one, dilute with water and note the exact amount used so that a comparative test with an arsenate can be made later.

**5. No Precipitate with Ammonium Molybdate Reagent.**—Add 2 cc.  $6n$   $\text{HNO}_3$  to 2 cc.  $\text{Na}_3\text{AsO}_3$  solution, warm and add an equal volume of ammonium molybdate reagent. No precipitate should form. Compare later with a similar test involving an arsenate.

### EXERCISES

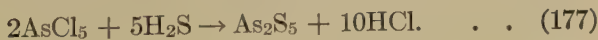
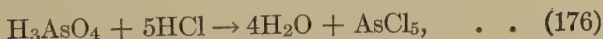
1. Show how an arsenite or arsenious acid can be used as a reducing agent.
2. If stannous chloride solution is added to a solution of an arsenite, made strongly acid with  $\text{HCl}$ , there will be a deposit of metallic arsenic. Give an explanation and the equation for the reaction.
3. If an arsenite were present in the filtrate from Group II of metals, does it follow that the solution could not contain  $\text{Ba}^{++}$  or  $\text{Ca}^{++}$ ?

### ARSENATE-ION, $\text{AsO}_4^{-3}$ (COLORLESS)

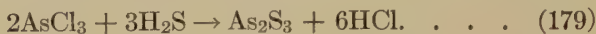
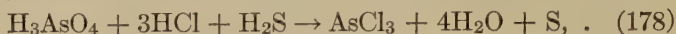
**1. Barium Arsenate,  $\text{Ba}_3(\text{AsO}_4)_2$ , and Calcium Arsenate,  $\text{Ca}_3(\text{AsO}_4)_2$ .**—Prepare the two precipitates from solutions of  $\text{Na}_3\text{AsO}_4$ . Which precipitating reagent is the more efficient? Test the solubility of the precipitates in  $6n$   $\text{HCl}$  and  $6n$   $\text{HNO}_3$ .

**2. Arsenic Acid,  $\text{H}_3\text{AsO}_4$ .**—Add 1 cc.  $3n$   $\text{HCl}$  to 3 cc. test solution of  $\text{Na}_3\text{AsO}_4$ . Slowly pass  $\text{H}_2\text{S}$  through the solution. If a precipitate does not form within five minutes, add more acid. Repeat the experiment by heating the solution nearly to boiling before passing the  $\text{H}_2\text{S}$  through. In the cold solution  $\text{As}_2\text{S}_5$  is slowly precipitated, while in the hot solution there is a mixture of  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_5$  and  $\text{S}$ . The reactions are:

In a cold solution,



This last reaction is very complete. What does this indicate about the solubility of  $\text{As}_2\text{S}_5$  in  $\text{HCl}$ ? In a hot solution,

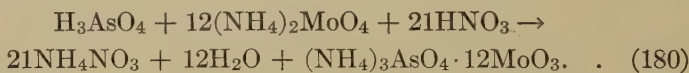


Compare the action of  $\text{H}_2\text{S}$  upon solutions of arsenites and arsenates.

**3. Silver Arsenate,  $\text{Ag}_3\text{AsO}_4$ .**—Add a solution of  $\text{AgNO}_3$  in excess to one of  $\text{Na}_3\text{AsO}_4$ . Describe the precipitate and compare with a similar test involving an arsenite. Is the precipitate soluble in  $6n$   $\text{HNO}_3$  or  $\text{NH}_4\text{OH}$ ?

**4. Magnesium Ammonium Arsenate,  $\text{MgNH}_4\text{AsO}_4$ .**—Prepare as you did with an arsenite. Compare results.

**5. Ammonium Arsenomolybdate,  $(\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3$ .**—Add 2 cc.  $6n$   $\text{HNO}_3$  to 2 cc.  $\text{Na}_3\text{AsO}_4$  solution. Warm and then add an equal volume of ammonium molybdate reagent. A yellow precipitate results, as shown by:



**6. Reduction of an Arsenate with  $\text{HI}$ .**—Add 1 cc.  $6n$   $\text{HCl}$  to 2 cc.  $\text{Na}_3\text{AsO}_4$  test solution. Now add 1 cc.  $\text{KI}$  solution and warm. The reaction is:



## EXERCISES

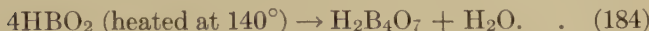
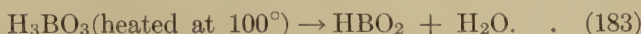
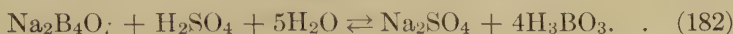
1. What experiments have you performed that have indicated a faint basic character of arsenic acid?
2. Compare the reactions of arsenites with those of arsenates.
3. Refer to Group II of cations and see what additional tests were emphasized in this section on arsenites and arsenates.

BORATE-ION,  $\text{BO}_3^{-3}$  (COLORLESS); ALSO  $\text{BO}_2^-$  AND  $\text{B}_4\text{O}_7^-$

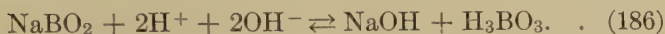
In making tests for borates the reactions may involve the orthoborate ion,  $\text{BO}_3^{-3}$ , the metaborate ion,  $\text{BO}_2^-$ , or the tetraborate ion,  $\text{B}_4\text{O}_7^-$ . Since the three ions are in equilibrium with each other as conditions are changed, it follows that a test for any



one of the ions is usually all that is necessary. The following reactions will show the interrelationships:



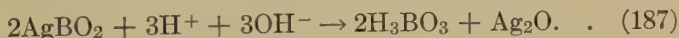
The boric acids are also interrelated by hydrolysis:



A solution of borax,  $\text{Na}_2\text{B}_4\text{O}_7$ , will, therefore, have all three ions in equilibrium.

**1. Barium Metaborate,  $\text{Ba}(\text{BO}_2)_2$ , and Calcium Metaborate,  $\text{Ca}(\text{BO}_2)_2$ .**—Obtain both of the precipitates by using two portions of the test solution of  $\text{Na}_2\text{B}_4\text{O}_7$ . Is the amount of precipitate the same with both reagents? Test the solubility in 6*N* HCl.

**2. Silver Metaborate,  $\text{AgBO}_2$ .**—Add 2 cc. of a test solution of  $\text{AgNO}_3$  to 3 cc. of a cold test solution of  $\text{Na}_2\text{B}_4\text{O}_7$ . Describe the precipitate. Write an equation for the reaction. Warm the precipitate. The brown precipitate is  $\text{Ag}_2\text{O}$  and is formed as follows:



**3. Orthoboric Acid,  $\text{H}_3\text{BO}_3$ .**—Place 3 cc. test solution of  $\text{Na}_2\text{B}_4\text{O}_7$  in an evaporating dish, concentrate nearly to dryness, cool, add 2 cc. 12*N*  $\text{H}_2\text{SO}_4$  and 2 cc. ethyl alcohol. Ignite the alcohol. What is the color of the flame? Is the color more prominent in any particular part of the flame?

The orthoboric acid which was formed by the addition of sulfuric acid reacts with the alcohol, forming a volatile compound as follows:



What metallic radicals might interfere with this test? Can you suggest a second purpose for using  $\text{H}_2\text{SO}_4$  with the borax solution, or in other words, would the use of HCl have been as satisfactory?

Make a second test with  $\text{H}_3\text{BO}_3$  by adding  $\text{HCl}$ , dropwise, to 3 cc. test solution of  $\text{Na}_2\text{B}_4\text{O}_7$  in an evaporating dish until it is just acid, and then add 2 drops in excess. Now dip a strip of turmeric paper into the solution and dry with some source of moderate heat. Do not dry over a flame; use a steam radiator or place the paper in direct sunlight or in a good draught of air. The dark red color of the dry turmeric paper will become a dark blue or black when a drop of  $\text{NaOH}$  solution is placed upon it. To emphasize the necessity of using a very slightly acid solution in this test, take a piece of turmeric paper and moisten with  $12n$   $\text{HCl}$ . What is the color change?

**4. Borax Beads.**—The use of borax beads has been discussed in metallic radical analysis and in detail in Plate VI.

### EXERCISES

1. Write the structural formula for  $\text{Na}_2\text{B}_4\text{O}_7$ .
2. Have you any experimental evidence to show which of the boric acids is the most soluble?
3. What do you think causes the green color of the alcohol flame when a borate is present?
4. What other compounds have you found that belong to the same class as  $(\text{C}_2\text{H}_5)_3\text{BO}_3$ ?
5. Does  $\text{H}_2\text{SO}_4$  displace  $\text{H}_3\text{BO}_3$  because it is a stronger acid?

CHROMATE-ION,  $\text{CrO}_4^{=}$  (YELLOW)

ALSO DICHROMATE-ION,  $\text{Cr}_2\text{O}_7^{=}$  (ORANGE-YELLOW)

The equilibrium between chromates and dichromates was discussed in the preliminary tests with the chromium-ion.

**1. Barium Chromate,  $\text{BaCrO}_4$ , and Calcium Chromate,  $\text{CaCrO}_4$ .** Review the proper method for precipitating  $\text{BaCrO}_4$  in the section on barium-ion. What is the value of  $\text{CaCl}_2$  as a precipitating agent for the chromate radical? Will the presence of soluble lead salts interfere with the precipitation of the  $\text{BaCl}_2$ - $\text{CaCl}_2$  group?

**2. Chromic Acid,  $\text{H}_2\text{CrO}_4$ .**—Review the tests made with chromic acid in connection with the identification of chromium.

**3. Silver Chromate,  $\text{Ag}_2\text{CrO}_4$ .**—Add, dropwise, a solution of  $\text{K}_2\text{CrO}_4$  to a test solution of  $\text{AgNO}_3$ . The brownish-red precipitate is  $\text{Ag}_2\text{CrO}_4$ . Write the equation. Test the solubility of the precipitate in  $6n$   $\text{HNO}_3$  and  $6n$   $\text{NH}_4\text{OH}$ .

## EXERCISES

1. Does it follow that a metal which is present in the negative radical will also give a test in the metallic procedure? (Consider a chromate and a borate.) In metallic analysis have you any indication as to whether chromium is in the metallic or the non-metallic radical?

2. How could you tell whether you had a chromate or a dichromate present?

3. Can you tell from the acidity or alkalinity of the original solution whether chromium is in the metallic or the non-metallic radical?

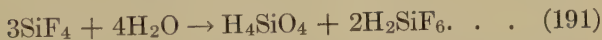
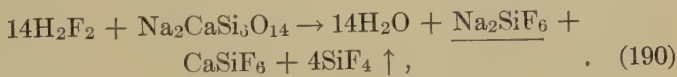
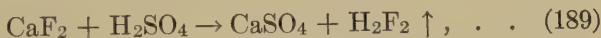
4. Summarize the solubilities of  $\text{BaCrO}_4$ ,  $\text{CaCrO}_4$  and  $\text{PbCrO}_4$  in acids.

5. Write the equations for the solution of  $\text{Ag}_2\text{CrO}_4$  in  $\text{NH}_4\text{OH}$ .

FLUORIDE-ION,  $\text{F}^-$  (COLORLESS)

1. **Barium Fluoride,  $\text{BaF}_2$ , and Calcium Fluoride,  $\text{CaF}_2$ .**—Add 2 cc.  $\text{BaCl}_2$  reagent to 2 cc. of a test solution of  $\text{NaF}$ . Is there any precipitate? Repeat, using  $\text{CaCl}_2$  reagent. Write the equation for the formation of  $\text{CaF}_2$ . Test the solubility of the precipitate in  $6n$   $\text{HCl}$  and in  $6n$  acetic acid.

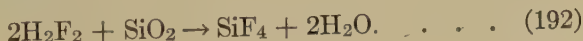
2. **Hydrofluoric Acid,  $\text{H}_2\text{F}_2$ .**—In a test tube place about 1 gram  $\text{CaF}_2$  and add  $12n$   $\text{H}_2\text{SO}_4$  until a thin paste results. Hold a platinum test wire with a film of water in the loop in the escaping vapors. (Do not breathe the fumes.) The opaqueness of the water film is due to the formation of  $\text{H}_4\text{SiO}_4$  or  $\text{H}_2\text{SiO}_3$ . The reactions are:



$\text{Na}_2\text{CaSi}_6\text{O}_{14}$  is the approximate formula of a soft soda glass.

Place a glass rod in the paste and loosely stopper the tube with a cotton plug. Now put the lower end of the tube in hot water for an hour. The part of the rod that was in the paste should be etched.

The reaction between  $\text{H}_2\text{F}_2$  and silica,  $\text{SiO}_2$ , is similar to that with glass and is shown by:



**3. Silver Fluoride,  $\text{AgF}$ .**—Add a solution of  $\text{AgNO}_3$  to a test solution of  $\text{NH}_4\text{F}$ . There should be no precipitate.

### EXERCISES

1. What other salt of calcium has the same solubility characteristics in acids as  $\text{CaF}_2$ ?

2. How does the strength of hydrofluoric acid compare with that of hydrochloric acid?

### OXALATE-ION, $\text{C}_2\text{O}_4^{=}$ (COLORLESS)

**1. Barium Oxalate,  $\text{BaC}_2\text{O}_4$ , and Calcium Oxalate,  $\text{CaC}_2\text{O}_4$ .**—Add 2 cc. of  $\text{BaCl}_2$  reagent to 3 cc. test solution of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . Repeat, using  $\text{CaCl}_2$  as the reagent. Test the solubility of the two precipitates in  $6n$   $\text{HCl}$  and  $6n$   $\text{HAc}$ . Refer to the solubility table and note how much more efficient  $\text{CaCl}_2$  should have been as the reagent for the precipitation of an oxalate. If your tests did not bring out this difference, revise the procedure so that the difference is shown.

**2. Oxalic Acid,  $\text{H}_2\text{C}_2\text{O}_4$ .**—Add  $6n$   $\text{H}_2\text{SO}_4$  to an equal volume of a test solution of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . Write the equation. Refer to the section on oxidation-reduction reactions for a discussion of the reducing action of oxalic acid. Also refer to the per cent dissociation of the acid in  $0.1n$  solution. What is the physical state of oxalic acid under ordinary conditions?

Take 1 cc.  $\text{KMnO}_4$  solution which is so dilute that only the faintest pink color remains. Add, dropwise, the solution of oxalic acid just prepared until the permanganate solution is decolorized. To show how necessary it is to have a very faintly colored solution in the bleaching tests, take a deeply colored  $\text{KMnO}_4$  solution and repeat the experiment. In the analysis of an unknown, it must be remembered that there will be only a few drops of solution available for bleaching purposes.

**3. Silver Oxalate,  $\text{Ag}_2\text{C}_2\text{O}_4$ .**—Slowly add a solution of  $\text{AgNO}_3$  to 3 cc. test solution of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . The white, curdy precipitate is  $\text{Ag}_2\text{C}_2\text{O}_4$ . Test its solubility in  $6n$   $\text{HNO}_3$  and  $6n$   $\text{NH}_4\text{OH}$ .

### EXERCISES

1. What substances besides oxalic acid will bleach a solution of  $\text{KMnO}_4$ ? Write the complete equation for the reaction between  $\text{KMnO}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$  in the presence of an excess of  $\text{H}_2\text{SO}_4$ .

2. Is there any advantage in using  $\text{H}_2\text{SO}_4$  instead of  $\text{HCl}$  in Question 1? How about  $\text{HNO}_3$ ?

3. In the reaction given in Question 1,  $\text{CO}_2$  is one of the products and it has been suggested that a test for  $\text{CO}_2$  can be used in confirming the presence of  $\text{H}_2\text{Ox}$ ; and, further, that finely divided solid  $\text{MnO}_2$  be used in place of a solution of  $\text{KMnO}_4$ . Explain any advantage in this procedure.

### PHOSPHATE-ION, $\text{PO}_4^{-3}$ (COLORLESS)

1. **Barium Phosphate,  $\text{Ba}_3(\text{PO}_4)_2$ , and Calcium Phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ .**—Prepare the two precipitates from test solutions of  $\text{Na}_2\text{HPO}_4$  and draw a conclusion as to their relative solubilities in water. Refer to solubility tables to substantiate your conclusion. Determine the solubility of either phosphate in  $6n$   $\text{HCl}$  and  $6n$   $\text{HAc}$ . If the phosphate does not dissolve entirely in the acid, take 2 cc. of a test solution of  $\text{Na}_2\text{HPO}_4$ , add 2 cc.  $6n$   $\text{HCl}$  and try to precipitate with  $\text{Na}_2\text{HPO}_4$ ? Add  $\text{NH}_4\text{OH}$  to the last solution, if prepared, until alkaline. Describe the result and give a full explanation.

2. **Phosphoric Acid,  $\text{H}_3\text{PO}_4$ .**—Test solutions of  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$  and  $\text{Na}_3\text{PO}_4$  with neutral litmus paper or a few drops of methyl orange indicator. Refer now to the per cent of primary, secondary and tertiary ionization of phosphoric acid and compare with the results you just obtained. Why use neutral litmus paper? Will hydrolysis affect the results? What is the physical state of  $\text{H}_3\text{PO}_4$  under ordinary conditions?

3. **Magnesium Ammonium Phosphate,  $\text{Mg}(\text{NH}_4)\text{PO}_4$ .**—Refer to the section on magnesium in Part II and review the method for obtaining this precipitate and its solubility in acids and bases. Refer also to tests made with the alkaline magnesium solution and with arsenious-ion and arsenic-ion. Summarize the results of your review.

4. **Ammonium Phosphomolybdate,  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ .**—Refer to the tests made with ammonium molybdate and arsenious-ion and arsenic-ion. Make a similar test with a solution of  $\text{Na}_2\text{HPO}_4$  and ammonium molybdate reagent. Be certain to have the solution acid with  $\text{HNO}_3$  and to have the reagent in large excess. Warm slightly. Make a summary of the molybdate reactions with  $\text{AsO}_4^{-3}$ ,  $\text{AsO}_4^{-3}$  and  $\text{PO}_4^{-3}$ .

5. **Silver Phosphate,  $\text{Ag}_3\text{PO}_4$ .**—Add a solution of  $\text{AgNO}_3$  to 3 cc. test solution of  $\text{Na}_2\text{HPO}_4$ . What is the color of the precipitate?



Test the solubility of the precipitate in  $6n$   $\text{NH}_4\text{OH}$  and  $6n$   $\text{HNO}_3$ . Refer to the section on silver arsenite and silver arsenate in Part III for comparison and make a summary of results.

### EXERCISES

1. Show by means of suitable equilibria any possible effect that hydrolysis may have on the  $[\text{H}^+]$  of solutions of the salts of phosphoric acid.

2. Try to obtain data which will show whether  $\text{H}_3\text{PO}_4$  is a weak acid because it ionizes to a small extent or whether insolubility is primarily involved in the problem.

3. In tabulated form, show the results of reactions between ions of  $\text{AsO}_3^{-3}$ ,  $\text{AsO}_4^{-3}$ ,  $\text{PO}_4^{-3}$  and the reagents ammonium molybdate, alkaline magnesium chloride solution and silver nitrate. Indicate which precipitates are soluble in  $6n$   $\text{HNO}_3$ .

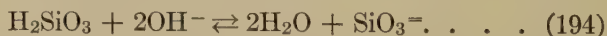
### SILICATE-ION, $\text{SiO}_3^-$ (COLORLESS)

1. **Barium Silicate,  $\text{BaSiO}_3$ , and Calcium Silicate,  $\text{CaSiO}_3$ .**—Obtain these precipitates by using a test solution of  $\text{Na}_2\text{SiO}_3$ . Test either precipitate for solubility in  $6n$   $\text{HCl}$  and  $6n$   $\text{HNO}_3$ .

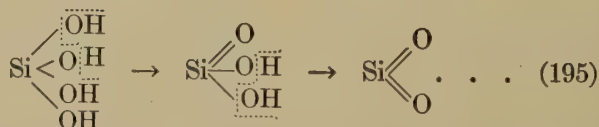
2. **Metasilicic Acid,  $\text{H}_2\text{SiO}_3$ .**—Test a solution of  $\text{Na}_2\text{SiO}_3$  with litmus paper. Explain the result. Add  $\text{HCl}$ , dropwise, to the solution until acid. A precipitate of  $\text{H}_2\text{SiO}_3$  will slowly form and will be either a well-consolidated gelatinous precipitate somewhat resembling that of  $\text{Al}(\text{OH})_3$ , or it will be in a colloidal suspension. The following is the reaction:



The metasilicate ion,  $\text{SiO}_3^-$ , evidently can exist only in an alkaline solution as shown by the following:



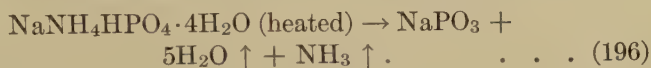
The silicic acids may be considered as hydrated forms of  $\text{SiO}_2$  and not hydroxides of the type of  $\text{NaOH}$ . The relationship is shown by:



Obtain sufficient  $\text{H}_2\text{SiO}_3$  to be filtered and washed once with hot water. Transfer to an evaporating dish and slowly dry.

Rapid heating will probably cause most of the contents of the dish to be lost by spattering. Is the residue soluble in 6*n* HCl or 12*n* HCl? The partially dehydrated substance, commonly referred to as silica gel, may appear in the complete analyses of samples as a part of the insoluble residue. What is the reaction of SiO<sub>2</sub> or SiO<sub>2</sub>·H<sub>2</sub>O with H<sub>2</sub>F<sub>2</sub>? Refer to tests with fluoride-ion. If the H<sub>2</sub>SiO<sub>3</sub> has resulted in a colloidal suspension, transfer the liquid to an evaporating dish, making certain that HCl is in excess, and evaporate to dryness as before. What other solid in this case will be present as well as SiO<sub>2</sub>·H<sub>2</sub>O?

Make a bead in the loop of a platinum test wire by heating some microcosmic salt, NH<sub>4</sub>NaHPO<sub>4</sub>·4H<sub>2</sub>O. Add a few grains of the mixture of SiO<sub>2</sub>·H<sub>2</sub>O and Na<sub>2</sub>SiO<sub>3</sub> obtained above and reheat. A characteristic stringy opaqueness is present throughout the bead due to the precipitation of SiO<sub>2</sub>. The reactions are:



It is to be noted that certain silicates cannot be readily decomposed by H<sub>2</sub>F<sub>2</sub> and require a special method of procedure which is given under the complete analysis of samples.

### EXERCISES

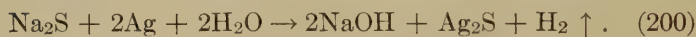
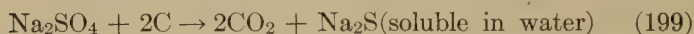
1. Which tests for SiO<sub>3</sub><sup>2-</sup> are similar to those for F<sup>-</sup> and which are different? Stating the question another way: Which tests for a silicate are applicable in the presence of a fluoride?
2. Would you consider silicon as having amphoteric characteristics?
3. Is the transition of metasilicic acid to orthosilicic acid, H<sub>4</sub>SiO<sub>4</sub>, one of hydrolysis? In your answer you must consider the results when a solution of Na<sub>2</sub>SiO<sub>3</sub> was tested by litmus paper. Discuss this question from as many points of view as possible.
4. We did not include a test of Na<sub>2</sub>SiO<sub>3</sub> with AgNO<sub>3</sub> in this section. Discuss the various features of this reaction.
5. Write an equation for the reaction between NaPO<sub>3</sub> and SiO<sub>2</sub>·H<sub>2</sub>O.

### SULFATE-ION, SO<sub>4</sub><sup>2-</sup> (COLORLESS)

**1. Barium Sulfate, BaSO<sub>4</sub>, and Calcium Sulfate, CaSO<sub>4</sub>.—** Use a test solution of Na<sub>2</sub>SO<sub>4</sub> and obtain both precipitates. Test the solubility of either precipitate in 6*n* HCl and 6*n* HNO<sub>3</sub>. If the barium salt contains a contamination of a fluoride there will also be

formed a precipitate of  $\text{BaSiF}_6$  which is insoluble in  $6n$  acid. Where does the Si come from? Why did the precipitate form only when the  $\text{BaSO}_4$  was precipitated?

Take 2 cc. test solution of  $\text{Na}_2\text{SO}_4$ , add 1 cc.  $6n$   $\text{HCl}$  and then 2 cc.  $\text{BaCl}_2$  reagent. Will the precipitate form in this acid solution? Do you recall any other radical of this group that will be precipitated under similar conditions? Make a fusion test with  $\text{BaSO}_4$  in what is known as the **Hepar test**, which is as follows: On a porcelain crucible cover, mix some  $\text{BaSO}_4$  with twice the volume of solid  $\text{Na}_2\text{CO}_3$  and an equal volume of powdered charcoal. Heat strongly for five minutes with a Meker type burner, and after cooling scrape off the residue and place on a clean silver coin. Moisten with a drop of water. A black stain of  $\text{Ag}_2\text{S}$  is a characteristic test and results as shown by the following reactions:



Sometimes it is more convenient to make the test in bead form by mixing the three solids, moistening with a drop of water and forming a ball in the loop on the end of a platinum wire. This should be heated in the reducing flame of a burner. Since some gas flames contain sulfur, this fact must be considered when the bead test is made. In place of the silver coin, the fused residue can be treated with a drop of  $\text{HCl}$  and the vapor tested for  $\text{H}_2\text{S}$  with a strip of filter paper moistened with a drop of  $\text{PbAc}_2$  solution.

This  $\text{Na}_2\text{CO}_3$  fusion will be frequently used in the complete analysis of unknowns in order to put insoluble residues into solution.

**2. Sulfuric Acid,  $\text{H}_2\text{SO}_4$ .**—What is the physical state of this acid under ordinary conditions? Is there any reason why the solubility tests of the precipitates studied in the preliminary work have been made with  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{HAc}$ , rather than with  $\text{H}_2\text{SO}_4$ ? Concentrated  $\text{H}_2\text{SO}_4$  is a dehydrating agent. Explain.

### EXERCISES

1. If  $12n$   $\text{HCl}$  is added dropwise to a nearly saturated solution of  $\text{BaCl}_2$ , a precipitate will result. What is this precipitate? How does this test differ from that in which a precipitate of  $\text{BaSO}_4$  was obtained? How could you

put into solution, without using acids or bases, the precipitate that was obtained with the HCl?

2. Make a summary of the sulfates insoluble in  $6n$  HCl. What sulfates can be formed in an alkaline solution?

3. Since  $\text{BaCO}_3$  is a precipitate, how can you account for the use of  $\text{Na}_2\text{CO}_3$  in the fusion of  $\text{BaSO}_4$ ?

#### TARTRATE-ION, $\text{C}_4\text{H}_4\text{O}_6^-$ (COLORLESS)

##### 1. Barium Tartrate, BaTr, and Calcium Tartrate, CaTr.—

Add  $\text{BaCl}_2$  and  $\text{CaCl}_2$  to portions of a test solution of sodium-potassium tartrate (Rochelle salt) or tartaric acid. Which precipitating reagent is the more efficient? Test the solubility of the precipitate in  $6n$  HCl and in  $6n$  HAc.

2. Tartaric Acid,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ .—What is the physical state of this acid under ordinary conditions? Heat tartaric acid or a tartrate on a crucible cover. What is the result? Note the characteristic odor during decomposition. Decompose another portion by means of  $16n$   $\text{H}_2\text{SO}_4$ . Note a characteristic frothing effect during the decomposition. Recall the bitartrate test that was used in the identification of  $\text{K}^+$  in Part II. How strong an acid is  $\text{H}_2\text{Tr}$ ?

##### 3. Silver Salts of Tartaric Acid and Their Decomposition.—

Add 2 cc. solution of  $\text{H}_2\text{Tr}$  to 3 cc. test solution of  $\text{AgNO}_3$ . No precipitate should form in the presence of free tartaric acid. Add 2 cc. test solution of NaKTr to 3 cc. test solution of  $\text{AgNO}_3$ . Write the equation for the reaction. Test the solubility of some of the precipitate in  $6n$  HCl and also in  $\text{NH}_4\text{OH}$ . Heat the ammoniacal solution. The final deposit is  $\text{Ag}^\circ$ . Describe the intermediate stages of the reduction. Silver tartrate does not deposit  $\text{Ag}^\circ$  when heated but in the ammoniacal solution there exists a silver ammonia complex which can be reduced by heating in the presence of the tartrate radical.

Deposit the  $\text{Ag}^\circ$  as a mirror by following this procedure: Take 5 cc. test solution of NaKTr, dilute in a test tube with 5 cc. water, add 5 drops NaOH solution and then  $\text{NH}_4\text{OH}$ , dropwise, until nearly all the precipitate has redissolved. Place this tube in a 300 cc. beaker of cold water, and warm. By the time the water has become tepid, a good mirror should be formed on the inside of the tube.

##### 4. Basic Magnesium Tartrate, $\text{Mg}_2(\text{OH})_2(\text{C}_4\text{H}_4\text{O}_6) \cdot \text{H}_2\text{O}$ .—

Precipitate this basic salt from a concentrated solution of tartaric

## PLATE V

A. The test for nickel in which the nickel dimethyl glyoxime has been concentrated in an ether layer. "Shell-pink" is the expression frequently applied to the color of the dissolved molecules.

B. The characteristic "ring test" for a nitrate. The solution being tested is in the upper layer and it contains a few drops of a solution of  $\text{FeSO}_4$  or  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ . The lower layer is  $36n$   $\text{H}_2\text{SO}_4$ . At the junction of the two liquids a faint brown or reddish-brown discoloration first appears and deepens upon standing for a few moments. The dark ring is ferrous nitrosyl sulfate,  $\text{Fe} \cdot \text{NO} \cdot \text{SO}_4$ .

C. The "ring test" for a nitrate which is made with a solution more concentrated than in B. The layer of precipitate may be quite thick and almost black.

D. The characteristic color of the permanganate ion. The solution is variously described as violet-red, reddish-violet, purple and also combinations of red and blue. Probably no solution changes color more with changes in concentration than that of permanganates. The photograph here shown was taken with a solution of  $0.0055m$   $\text{KMnO}_4$ . With higher concentrations the solution becomes a deeper blue or violet and with greater dilution the red color predominates, and a very dilute solution is pink.

E. A small amount of iodine dissolved in  $\text{CS}_2$  gives a pink or red color.

F. Bromine in small amounts colors  $\text{CS}_2$  a light yellow.

G. When much iodine is present in  $\text{CS}_2$  the color is a very dark red and may be almost black when very concentrated. More  $\text{CS}_2$  should be added in this case so that the red can be distinctly seen.

H. A yellowish-brown results when there is much bromine in  $\text{CS}_2$ . A caution is given that a light coloration in the  $\text{CS}_2$  layer does not necessarily indicate bromine and a dark coloration iodine.

I. Perchromic acid molecules are very unstable and have a characteristic blue color. In this solution the blue color is indistinct because the molecules are distributed throughout the solution.

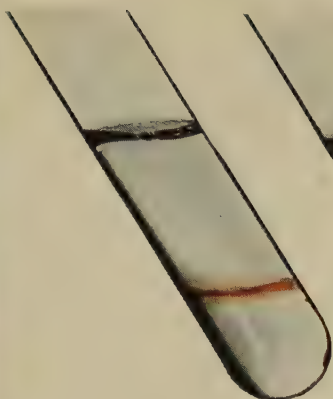
J. Ether has been added to the solution in I and, after mixing, the liquids are allowed to settle. The perchromic acid is concentrated in the upper ether layer.



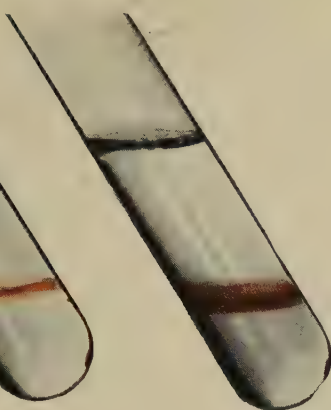
PLATE V



A



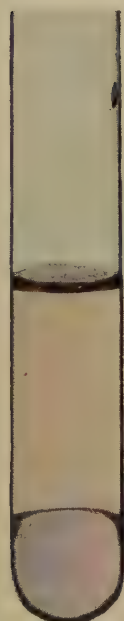
B



C



D



E



F



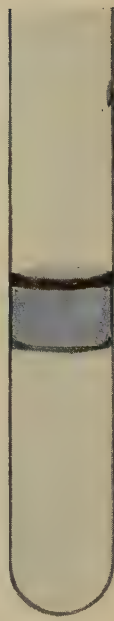
G



H



I



J



acid by means of ammoniacal magnesium chloride solution. The precipitate deposits slowly and its formation may be hastened by the addition of 95 per cent alcohol. Can a test for  $Mg^{++}$  be obtained in the presence of a tartrate?

### EXERCISES

1. Make a complete list of the radicals in this group that have been more efficiently precipitated with  $CaCl_2$  than with  $BaCl_2$ .
2. Does the presence of  $H_2Tr$  prevent the precipitation of  $Ag_2Tr$  when a solution of  $AgNO_3$  is added to that of  $NaKTr$ , or will the presence of any acid have a similar effect? Write the equation for the reaction.
3. If  $H_2Tr$  prevents the precipitation of  $Ag_2Tr$  in Exercise 2, how can it be removed so that precipitation will take place?

### THE "PREPARED SOLUTION"

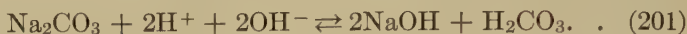
It was emphasized at the beginning of the preliminary tests with Group II anions that when the group reagent,  $BaCl_2$ - $CaCl_2$ , is added in the course of an analysis it is necessary that the solution should not contain metallic radicals other than  $K^+$ ,  $Na^+$  and  $NH_4^+$  as well as the non-metallic radicals of Group I anions.

If the solution that you are analyzing contains Group II anions only, it will contain sodium, potassium or ammonium salts of the acid radicals of the group or the free acids themselves. When the solution under consideration is not limited to Group II anions, in order to remove the conflicting radicals, take 5 cc. of the solution and place in a 300-cc. flask. Add 1 gram of solid  $Na_2CO_3$ , dilute with 100 cc. water and boil for five minutes. Filter, wash the precipitate once with hot water and combine the filtrate and washings. To determine whether the action is complete, take 3 cc. of the filtrate, add 3 cc. of a solution of  $Na_2CO_3$  and bring to a boil. If a precipitate forms, return this side test to the main filtrate, place all of the liquid in the flask again, add another gram of solid  $Na_2CO_3$  and boil for five minutes. Remove the precipitate as before and again test filtrate for completeness of removal of metallic radicals.

In order to remove the excess  $Na_2CO_3$  which is now in solution, slowly add in small portions 16*N*  $HNO_3$  until the solution is acid. Boil the solution until  $CO_2$  is eliminated. Test for the presence of  $CO_2$  in the vapor; do not guess. Make another test for the acidity of the solution, and if it is found not to be faintly acid yet,

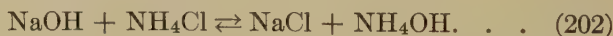
add some  $\text{HNO}_3$  and again boil for a minute or two. The prepared solution should have these characteristics: No heavy metals present; no Group I anions present, which includes the  $\text{CO}_3^{=}$  from the  $\text{Na}_2\text{CO}_3$ ; faintly acid with  $\text{HNO}_3$ .

In giving an explanation of the reactions involved in the preparation of the Special Prepared Solution, we first consider the hydrolysis of the reagent, which is shown in the following:

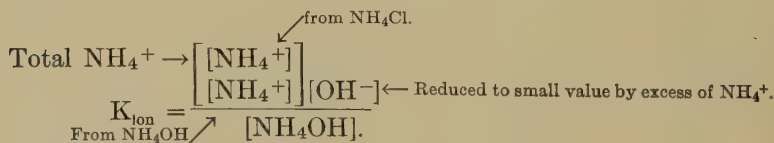


There are present, therefore, in the solution, the  $\text{OH}^-$  and  $\text{CO}_3^{=}$  radicals for the precipitation of the heavy metals. By referring to the solubility tables it will be found that all of the metallic radicals, except  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ , form insoluble hydroxides or carbonates in a neutral or alkaline solution not containing  $\text{NH}_4\text{OH}$  or ammonium salts. In some instances, both the hydroxide and the carbonate are insoluble.

The presence of ammonium salts in the solution, especially in large quantities, calls for special consideration. The double decomposition or metathetical reaction, between  $\text{NaOH}$  and  $\text{NH}_4\text{Cl}$  liberates  $\text{NH}_4\text{OH}$  as shown by:



The  $\text{OH}^-$  from this source will precipitate hydroxides as well as from the  $\text{NaOH}$ , but its value will be reduced to a small amount in the presence of  $\text{NH}_4\text{Cl}$  by the common-ion effect.



One effect of boiling the solution is the decomposition of the  $\text{NH}_4\text{OH}$  into  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . The combined effect, therefore, of an excess of  $\text{NH}_4\text{Cl}$  or other ammonium salt is to use up the  $\text{NaOH}$  which has been formed by hydrolysis and either to decompose the resulting  $\text{NH}_4\text{OH}$  or to render its precipitating value ineffective.

Where  $\text{NH}_4^+$  has been determined in the metallic analysis it will be necessary, therefore, in making the Prepared Solution, after

filtering off the first precipitate, to concentrate the solution in an evaporating dish to one-third of its original volume, add another gram of solid  $\text{Na}_2\text{CO}_3$  and boil for five minutes. The final solution, which has been made acid with  $\text{HNO}_3$ , boiled, cooled and refiltered, may now contain only the metallic radicals  $\text{Na}^+$ ,  $\text{K}^+$  and the acid radicals of Group II and succeeding groups. Boiling with  $\text{HNO}_3$  removed Group I anions.

Where the solution to be analyzed contains metals in the non-metallic radical, principally metals that belong to the class which can form amphoteric hydroxides, their removal by the  $\text{Na}_2\text{CO}_3$  treatment is not complete. In the exercises which follow, some of the questions suggest the main difficulties. A Prepared Solution which is made from the filtrate of Group II cations will eliminate most of the conflicts to which your attention has been directed.

Where a solution contains a large excess of  $\text{Cu}^{++}$ , its removal in the Prepared Solution may be incomplete, especially where ammonium salts have been present. Explain. The final solution will in this case be colored. The copper can be removed by taking the final solution, which is faintly acid, passing  $\text{H}_2\text{S}$  through and filtering off the  $\text{CuS}$  which has resulted. The excess  $\text{H}_2\text{S}$  must be thoroughly removed by boiling. Why?

### EXERCISES

1. Why is the prepared solution made acid with  $\text{HNO}_3$  instead of  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ ? Would  $\text{HAc}$  be permissible?
2. Why not allow the solution to remain alkaline with  $\text{NH}_4\text{OH}$ ? (Remember that this solution may stand several hours before it is finally used.)
3. Will amphoteric substances be completely removed by the  $\text{Na}_2\text{CO}_3$  process. Explain in full.
4. Make a list of ampholytes that may be present when the Prepared Solution is made.
5. What will be the effect of the  $\text{Na}_2\text{CO}_3$  treatment upon chromates and dichromates?
6. If a permanganate is present, how will it react in making a prepared solution?



## SUMMARY OF REACTIONS OF THE ACIDS AND ACID RADICALS IN THE BARIUM CHLORIDE-CALCIUM CHLORIDE GROUP THAT ARE OF IMPORTANCE IN ANALYTICAL PROCEDURE

We have seen that the analysis of the  $\text{BaCl}_2$ - $\text{CaCl}_2$  group of anions begins with a preliminary inspection of the original solution; this is followed by a careful consideration of the results of the analysis for metallic radicals. A light yellow or orange solution will suggest the presence of  $\text{CrO}_4^{=}$  or  $\text{Cr}_2\text{O}_7^{=}$ . It has been pointed out, however, that the colors of ions can be rendered ineffective (see complete analysis for cations).

During the  $\text{H}_2\text{S}$  precipitation, it is important to follow any color changes as reduction and precipitation occur. The chromate or dichromate ion changes to the green of  $\text{Cr}^{+3}$ . The rapid precipitation of  $\text{As}_2\text{S}_3$  from an arsenite and the slow precipitation of  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{S}_5$  from an arsenate is difficult to follow because there are other yellow precipitates which may also be present. The intermediate precipitates of  $\text{Hg}^{++}$  and  $\text{Sb}^{+3}$  are especially conflicting. The presence of  $\text{As}^{+3}$  or  $\text{Sb}^{+3}$  in Group II metallic analysis does not indicate anything whatever about their original condition in the solution. None of the other radicals in the  $\text{BaCl}_2$ - $\text{CaCl}_2$  group are reduced by  $\text{H}_2\text{S}$ .

It was shown in the preliminary tests that the  $\text{BaCl}_2$ - $\text{CaCl}_2$  reagent cannot be added to an alkaline solution containing the radicals of this group without first removing all metallic radicals with the exception of those of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ . Unless the conflicting metallic radicals are removed there will be an immediate precipitate formed with the acid radicals of this group as soon as the solution is made alkaline, without the addition of any  $\text{BaCl}_2$ - $\text{CaCl}_2$  reagent. The majority of the conflicting metallic radicals we found could be removed by preparing a special solution known as the Prepared Solution. The presence of several of the negative radicals of Group I of anions was also found to interfere with this group by precipitating the group reagent. Consequently the volatile group of acids must also be eliminated before the  $\text{BaCl}_2$ - $\text{CaCl}_2$  reagent is added.

By reviewing the silver salts of the acid radicals of this group we find that several are very characteristic, and by taking some of the Prepared Solution which has been made slightly acid with

$\text{HNO}_3$ , then adding  $\text{AgNO}_3$  and neutralizing with  $n \text{ NH}_4\text{OH}$ , a precipitate will result that is a useful preliminary test.

TABLE XVII  
SILVER SALTS OF GROUP II ANIONS

Acid Radical	Precipitate with $\text{AgNO}_3$	Characteristics of Precipitate
$\text{AsO}_3^{-3}$	<u><math>\text{Ag}_3\text{AsO}_3</math></u>	yellow
$\text{AsO}_4^{-3}$	<u><math>\text{Ag}_3\text{AsO}_4</math></u>	reddish-brown
$\text{BO}_3^{-3}$	<u><math>\text{Ag}_3\text{BO}_3</math></u>	white $\rightarrow$ gray
$\text{CrO}_4^{-}$	<u><math>\text{Ag}_2\text{CrO}_4</math></u>	dark reddish-brown
$\text{F}^-$	.....	.....
$\text{C}_2\text{O}_4^{-}$	$\text{Ag}_2\text{C}_2\text{O}_4$	curdy white
$\text{PO}_4^{-3}$	$\text{Ag}_3\text{PO}_4$	yellow
$\text{SiO}_3^{-}$	.....	.....
$\text{SO}_4^{-}$	$\text{Ag}_2\text{SO}_4$	white
	(Only in conc. sol.)	
$\text{C}_4\text{H}_4\text{O}_6^{-}$	$\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$	white
	(Only in neutral sol.)	

In considering the effectiveness of the  $\text{BaCl}_2$ - $\text{CaCl}_2$  reagent, the tests have shown that the  $\text{BaCl}_2$  is especially effective for the precipitation of  $\text{SO}_4^{-}$  and  $\text{CrO}_4^{-}$ , while  $\text{CaCl}_2$  is more efficient when  $\text{Ox}^-$ ,  $\text{F}^-$  and  $\text{Tr}^-$  are concerned.

The group precipitate was found to be soluble in  $6n \text{ HCl}$  with the exception of the sulfates. With some of the components we found that solution took place slowly. The reverse process, however, can be made very effective; that is, by making the solution acid with  $\text{HCl}$  before adding the group reagent, the only precipitate will be of the sulfates.

It is necessary to emphasize the similarity between the tests with the magnesia mixture and the ammonium molybdate reagent where  $\text{AsO}_4^{-3}$  and  $\text{PO}_4^{-3}$  are concerned. This means that these two tests for phosphates cannot be made in the presence of arsenates. An efficient method of eliminating the arsenate radical is to make some of the Prepared Solution acid with  $\text{HCl}$  and then completely reduce and precipitate with  $\text{H}_2\text{S}$ .

TABLE XVIII

## THE OUTSTANDING INDIVIDUAL TESTS FOR GROUP II ANIONS

Radical	Test
$\text{AsO}_3^{-3}$ .....	Rapid precipitation with $\text{H}_2\text{S}$ .
$\text{AsO}_4^{-3}$ .....	Slow precipitation with $\text{H}_2\text{S}$ . Ppt. with ammonium molybdate or magnesia reagents.
$\text{BO}_3^{-3}$ .....	Colored alcohol flame or characteristic color with turmeric paper.
$\text{CrO}_4^{-}$ .....	Blue colored solution with $\text{H}_2\text{O}_2$ and ether in acid solution.
$\text{F}^{-}$ .....	Liberation of $\text{H}_2\text{F}_2$ in the presence of conc. $\text{H}_2\text{SO}_4$ .
$\text{C}_2\text{O}_4^{-}$ .....	Reducing action on $\text{KMnO}_4$ solution.
$\text{PO}_4^{-3}$ .....	In the absence of $\text{AsO}_4^{-3}$ , the formation of a ppt. with ammonium molybdate or magnesia reagents.
$\text{SiO}_3^{-}$ .....	Liberation of $\text{SiF}_4$ in the presence of conc. $\text{H}_2\text{SO}_4$ and a fluoride; also ppt. of $\text{SiO}_2$ by fusing with microcosmic salt.
$\text{SO}_4^{-}$ .....	Precipitation from a slightly acid solution by $\text{BaCl}_2$ .
$\text{C}_4\text{H}_4\text{O}_6^{-}$ .....	Formation of characteristic silver mirror, and decomposition by heat with charring.

## PROCEDURE FOR THE ANALYSIS OF A PRACTICE SOLUTION CONTAINING ACID RADICALS OF GROUP II, THE BARIUM CHLORIDE-CALCIUM CHLORIDE GROUP

It is assumed that Group I of anions is absent and that the solution is slightly acid with  $\text{HNO}_3$ . The metallic radicals that may be present are not limited to  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ .

**Preliminary Test with  $\text{AgNO}_3$  in a Prepared Solution.**—Take 5 cc. of the solution for analysis and make a Prepared Solution as previously outlined on page 259. Concentrate the solution to 20 cc., cool and test for acidity. If necessary add, dropwise,  $\text{HNO}_3$  until acid. Take 5 cc. of this solution, add 3 cc.  $\text{AgNO}_3$  reagent, then make just alkaline with  $\text{NH}_4\text{OH}$ . Observe the color of the precipitates of silver salts. Warm slightly and note any changes. Refer to page 263 for characteristics of the precipitates of the silver salts.

**Identification of Arsenites.**—Take 2 cc. of the original solution, add 2 cc. water, heat to boiling and pass  $\text{H}_2\text{S}$  through the solution.

A **yellow precipitate** which forms **rapidly** is  $\text{As}_2\text{S}_3$  and indicates the presence of an arsenite unless  $\text{As}^{+3}$  is present. Make a similar test with 2 cc. of the Prepared Solution.<sup>b</sup> An immediate precipitate of  $\text{As}_2\text{S}_3$  will confirm arsenites.

**Identification of Arsenates.**—When the tests are made for arsenites, a very **slow precipitation** of **yellow sulfides** suggests the presence of an arsenate<sup>c</sup>. When there is an immediate precipitation of  $\text{As}_2\text{S}_3$ , the slow formation of  $\text{As}_2\text{S}_5$  will, of course, be obscured.

Make a confirmatory test in the original solution for an arsenate by using either the ammonium molybdate reagent<sup>d</sup> or the ammoniacal magnesium chloride reagent<sup>e</sup> as outlined in the preliminary tests. Since phosphates will also give similar precipitates with these two reagents, it is necessary to make another confirmatory test. This is done by using the precipitate which was obtained with the magnesia mixture. Filter this precipitate, wash once with cold water and pour 3 cc.  $\text{AgNO}_3$  solution containing 4 drops  $\text{HAc}$  over the precipitate. Catch the solution that runs through and pour it over the precipitate a second time. Wash the precipitate once with water, and reject the filtrate and washings. A reddish-brown precipitate on the filter paper indicates the presence of  $\text{Ag}_3\text{AsO}_4$ , and this finally confirms an arsenate in the presence of a phosphate.<sup>f</sup>

**Identification of Borates.**—Make a flame test<sup>g</sup> with 2 cc. of the original solution as outlined in the preliminary tests. This test, resulting in a **green flame** is conclusive only if it is known, from a preceding cation analysis, that  $\text{Cu}^{++}$  is absent. Where the absence of copper is not certain repeat the test by using the same amount of Prepared Solution<sup>h</sup>. The **turmeric paper test** can be used if great care is taken to prevent excess acidity.<sup>i</sup> The flame test is usually much more conclusive.

**Identification of Chromates.**—Add  $\text{NH}_4\text{OH}$  to 2 cc. of the Prepared Solution until it is alkaline, then 1 cc.  $\text{BaCl}_2\text{-CaCl}_2$  reagent<sup>j</sup>. The yellow color of  $\text{BaCrO}_4$  is a preliminary test for a chromate. When the cation analysis has preceded these tests it has been pointed out that the characteristic **reduction of a chromate or dichromate by  $\text{H}_2\text{S}$**  is also a valuable preliminary test. Further to confirm a chromate, make the  $\text{H}_2\text{O}_2$ -ether test in the original or Prepared Solution giving **perchromic acid** as previously outlined on page 177.



**Identification of Fluorides.**—Evaporate 3 cc. of the original solution about to dryness, place in a lead dish, add an equal volume of fine sand<sup>k</sup> and 2 cc. 16*n* H<sub>2</sub>SO<sub>4</sub>. Warm gently under the hood and test the vapors with a water film in the loop of a platinum wire. The characteristic opaqueness due to the formation of H<sub>2</sub>SiO<sub>3</sub> or H<sub>4</sub>SiO<sub>4</sub> confirms a fluoride. The presence of silicates does not interfere with this test but would, in fact, make the addition of sand unnecessary. The etching test cannot be used for fluoride where silicates may be present.

**Identification of Oxalates.**—Place 3 cc. Prepared Solution in a test tube, make just alkaline with NH<sub>4</sub>OH, then add, dropwise, 6*n* HAc until acid. Precipitate with a saturated solution of CaSO<sub>4</sub>. Allow precipitate to settle, wash once by decantation and decant off the liquid. Add 2 cc.<sup>l</sup> 6*n* H<sub>2</sub>SO<sub>4</sub> and warm gently. Prepare 1 cc. KMnO<sub>4</sub> solution so that it has the faintest pink color. Add, dropwise, to this pink solution, the acid solution just prepared. A decolorizing of the KMnO<sub>4</sub> solution indicates an oxalate.<sup>m</sup>

**Identification of Phosphates.**—Where arsenates have been found to be present, they must be removed before the phosphate test can be made. Recall that an arsenate is not necessarily removed in the regular preparation of the Prepared Solution. Take 3-5 cc.<sup>n</sup> of the original solution, add 2 cc. 6*n* HCl, dilute to 20 cc. with water, reheat to boiling and completely precipitate with H<sub>2</sub>S. Filter and discard the precipitate of As<sub>2</sub>S<sub>3</sub>, As<sub>2</sub>S<sub>5</sub> and S, and test filtrate for completeness of precipitation. Wash precipitate once with hot water and combine filtrate and washings. Boil to eliminate H<sub>2</sub>S and concentrate to 6 cc. Cool, filter<sup>o</sup> and divide into two parts. Make the tests with ammonium molybdate reagent and magnesia mixture as outlined in the sections on AsO<sub>4</sub><sup>-3</sup> and PO<sub>4</sub><sup>-3</sup>. The characteristic precipitate of MgNH<sub>4</sub>PO<sub>4</sub> or (NH<sub>4</sub>)<sub>3</sub> PO<sub>4</sub>·12MoO<sub>3</sub> confirms phosphates.

Where arsenates are not present, the tests for phosphates can be made in the original solution.

**Identification of Silicates.**—Evaporate 1 cc. of the original solution to dryness. Make the fusion test with microcosmic salt as outlined on page 255. The characteristic opaqueness due to the precipitation of SiO<sub>2</sub> indicates silicates.

Where fluorides have been found to be absent, evaporate 3 cc. of the original solution to dryness and either add H<sub>2</sub>F<sub>2</sub> solution or



mix a little  $\text{CaF}_2$  and concentrated  $\text{H}_2\text{SO}_4$  with the dried residue. In either case  $\text{SiF}_4$  will be given off and can be confirmed by the etching test or with a film of water as outlined on page 251.

**Identification of Sulfates.**—Take 3 cc. of the Prepared Solution, make alkaline with  $\text{NH}_4\text{OH}$ , then add  $3n$   $\text{HCl}$  in slight excess. Now add, dropwise, the  $\text{BaCl}_2$ - $\text{CaCl}_2$  reagent until precipitation is complete. Allow to settle for five minutes and decant off the liquid. Wash once with water by decantation and decant off liquid. Remove most of the precipitate and make the Hepar test as outlined on page 256. The black  $\text{Ag}_2\text{S}$  stain indicates sulfates.

To the small amount of precipitate remaining in the test tube, add 3 drops  $6n$   $\text{HCl}$ . The insolubility of the precipitate in  $\text{HCl}$  also confirms the presence of sulfates. The formation of a precipitate of  $\text{BaSO}_4$  with  $\text{BaCl}_2$  in a solution containing a moderate concentration of  $\text{HCl}$  is a very sure indication of the presence of a sulfate.<sup>p</sup>

**Identification of Tartrates.**—Since the presence of organic material which chars upon heating is limited in this solution to tartrates, a small amount of the original solution, evaporated to dryness and either ignited or heated with 2 drops of concentrated  $\text{H}_2\text{SO}_4$ , will indicate tartrates by the **charring**<sup>q</sup> and **characteristic odor**. The mirror test described on page 257 can be used as a confirmatory test.

#### NOTES ON THE PROCEDURE FOR THE ANALYSIS OF A PRACTICE SOLUTION CONTAINING GROUP II ANIONS

- a. If the solution is only slightly acid, add 2 drops  $6n$   $\text{HCl}$ .
- b. The solution must be acid. Since the Prepared Solution was left in an acid condition due to a slight excess of  $\text{HNO}_3$ , water is added to eliminate the effect of too concentrated a solution of this oxidizing agent upon  $\text{H}_2\text{S}$ . If the Prepared Solution has been standing for some time and is faintly acid, 3 drops of  $6n$   $\text{HCl}$  can be added before passing through the  $\text{H}_2\text{S}$ .
- c. The acidity with  $\text{HCl}$  must be increased in the test for an arsenate. Add 10 drops more of  $6n$   $\text{HCl}$  before passing through  $\text{H}_2\text{S}$ .
- d. Again let the fact be emphasized that the solution must be quite strongly acid with  $\text{HNO}_3$ , that the volume of reagent must be in large excess and that it may be necessary to warm the solution. It must not be boiled, however.
- e. The solution is made ammoniacal before using the magnesia mixture because the test is performed in an alkaline solution. If the solution to be tested is quite acid, the  $\text{NH}_4\text{OH}$  of the magnesia mixture may be neutralized, and the final acid condition of the solution would preclude the formation of any  $\text{MgNH}_4\text{AsO}_4$ .

f. The precautions in making a test for an arsenate in the presence of an arsenite and a phosphate may seem to be never-ending, but it is necessary to give another conflicting possibility. Suppose that there is so much phosphate present that the yellow  $\text{Ag}_3\text{PO}_4$  obscures the reddish-brown  $\text{Ag}_3\text{AsO}_4$ . To be certain of the presence of an arsenate where the silver precipitate is yellow and without the least suggestion of a red precipitate, pour over the yellow precipitate 3 cc. 6*n* HCl. Pour the solution which passes through over the filter paper again. Wash with 3 cc. water. To the combined filtrate and washings, add 1 cc. KI solution and 3 cc. colorless  $\text{CS}_2$ . Shake the mixture, and after settling note any pink color in the  $\text{CS}_2$  layer, which is due to dissolved  $\text{I}_2$ . A phosphate will not reduce KI solution. Recall a similar test that was made when a chromate was identified in metallic analysis, and avoid letting the solution stand. There is always danger of I being formed when KI is in contact with an acid for more than a few minutes.

g. Use only ethyl alcohol or one of the denatured substitutes. Never use wood alcohol on account of its injurious physiological effects.

h. It is better to make the borate test in the original solution when possible, because there are continued losses as the number of operations increases.

i. Another disadvantage of the turmeric paper test is that oxidizing agents will discolor the paper and obscure the borate test. They should therefore be removed before the test is made. Chromates can be removed by adding solid  $\text{Na}_2\text{SO}_3$  to 3 cc. of the original solution, then adding 2 cc. 6*n* HCl and bringing to a boil. A prepared solution can now be made by adding  $\text{Na}_2\text{CO}_3$  in excess as in the usual procedure.

j. Do not use any combination of  $\text{BaCl}_2$  and  $\text{CaCl}_2$  for the precipitating reagent. Take some that is prepared according to instructions given in Part V.

k. The presence of the fine sand (not larger than 100 mesh) supplies a silicate for the  $\text{H}_2\text{F}_2$  to decompose, forming  $\text{SiF}_4$ . Then



l. This is the maximum amount of acid to be added. The resulting oxalic acid solution must be kept concentrated.

m. Calcium tartrate is precipitated by  $\text{CaSO}_4$ , but tartaric acid is not a reducing agent. Calcium arsenite is not precipitated, hence arsenious acid, the other reducing agent in the group, is not present at this point.

n. The amounts which are suggested are based upon a 25-30 cc. sample of solution of the usual strength as outlined in the preliminary discussion of laboratory procedure. In making this phosphate test, 5 cc. will give more conclusive results, if this amount of solution is available.

o. Free sulfur may have formed during the elimination of  $\text{H}_2\text{S}$  by boiling.

p. A precipitate of  $\text{BaSiF}_6$  may be formed with the sulfate if there is a contamination of fluosilicate. This precipitate can be decomposed by heating with concentrated  $\text{H}_2\text{SO}_4$  according to the following:



q. A dark ignited residue is not limited to charring. Many metallic salts

will give black oxides upon ignition, as  $\text{Fe}_2\text{O}_3$ . A residue containing a tartrate, when evaporated to dryness, will char and "sponge up" when concentrated  $\text{H}_2\text{SO}_4$  is added. There is also the characteristic "burnt sugar" odor during the decomposition.

### OPTIONAL TESTS

The  $\text{BaCl}_2\text{-CaCl}_2$  group can be divided into two parts by adding  $6n$  HAc to the combined precipitate. The precipitates of  $\text{BaCrO}_4$ ,  $\text{CaF}_2$ ,  $\text{CaOx}$  and  $\text{BaSO}_4$  will remain in the residue. Conversely, if the prepared solution is acid by an excess of HAc, then the  $\text{BaCl}_2\text{-CaCl}_2$  reagent will precipitate only the salts that have just been mentioned. Since most of the tests are individual ones and are made in the original or prepared solution, this subdivision is hardly necessary.

If the prepared solution is not made acid with  $\text{HNO}_3$  or  $\text{HCl}$  and then boiled, members of the volatile group will still be present. Now, by adding the  $\text{BaCl}_2\text{-CaCl}_2$  reagent to the prepared solution made acid with  $\text{HCl}$ , a new grouping of radicals will result. A still different grouping will be obtained if HAc is used in place of  $\text{HCl}$ . A still further modification can be made by making the prepared solution acid with  $\text{HNO}_3$ , but not boiling to drive off the volatile group, then adding  $\text{AgNO}_3$  reagent. A group consisting of silver salts insoluble in  $\text{HNO}_3$  will result as Group I. The  $\text{BaCl}_2\text{-CaCl}_2$  group can then be precipitated with variations as outlined.

The borate test can be made more effective if turmeric solution is used in place of turmeric paper. The test must be made under carefully controlled conditions, however, to have much value.

## CHAPTER IV

### GROUP III.—THE SILVER NITRATE GROUP

IODIDE, $I^-$	FERRICYANIDE, $[Fe(CN)_6]^{-3}$
BROMIDE, $Br^-$	FERROCYANIDE, $[Fe(CN)_6]^{-4}$
CHLORIDE, $Cl^-$	THIOCYANATE, $SCN^-$

This group of anions is characterized in the absence of Group I by forming precipitates with  $AgNO_3$  in a solution which is acid with  $HNO_3$ .

#### PRELIMINARY TESTS

##### IODIDE-ION, $I^-$ (COLORLESS)

**1. Silver Iodide,  $AgI$ .**—Slowly add a solution of  $AgNO_3$  to 3 cc. test solution of  $KI$ . Describe the precipitate. Filter and wash once with water. Pour 3 cc.  $6N$   $NH_4OH$  over the precipitate. Catch the solution in a test tube and again pour it over the filter. Does the precipitate dissolve? Make the filtrate acid with  $HNO_3$ . Describe the result and give your deduction.

**2. Displacement of Iodide-ion by Molecular Chlorine,  $Cl_2$ , and Molecular Bromine,  $Br_2$ .**—Place 1 cc. test solution of  $KI$  in a test tube, dilute with 1 cc. water, add 1 drop  $3N$   $HCl$  and 1 cc. saturated chlorine water.<sup>1</sup> Now add 2 cc. colorless  $CS_2$  and thoroughly shake the mixture for about ten seconds. Allow to settle and note the color of the  $I_2$  dissolved in the  $CS_2$  layer. Write the equation for the displacement. Vary the concentration of  $I_2$  in  $CS_2$  so that you become familiar with the change of color from a light pink to a dark red (see Plate V, *E* and *G*). Note especially that the

<sup>1</sup>The experiments with the halides and chlorine water will be of little value unless the tests are made under similar conditions. Chlorine water should be approximately saturated, and the best source of the gas is the steel bomb containing liquefied chlorine gas. By this means, a small amount of chlorine water can be supplied at frequent intervals and in a fairly uniform concentration.

color ranges from pink to dark red and not from yellow to brown. What other solvents might be used in place of  $\text{CS}_2$ ?

Repeat the experiment with a KI solution, using a saturated solution of bromine water. Is the identification as conclusive in this case as with the chlorine water? Give two reasons for this difference.

To show how the iodide-ion can be completely displaced, take a small separatory funnel and repeat the experiment with KI solution,  $\text{HCl}$ , chlorine water and  $\text{CS}_2$ . After shaking the mixture and permitting to settle, carefully draw off the  $\text{CS}_2$  layer from the bottom and add another 2 cc. of  $\text{CS}_2$  to the contents of the separatory funnel. Now add more chlorine water and repeat the displacement and extraction until the  $\text{CS}_2$  layer is practically colorless.

### 3. Adsorption of Dispersed Iodine by a Starch Suspension.—

Dissolve a small crystal of iodine in 2 cc. KI test solution. Add this to 1 cc. starch suspension which has been diluted with 10 cc. water. The blue color is due to finely divided particles of iodine being taken up by the gelatinous surface of the starch granules. The solution will appear almost black if too concentrated. Dilute if necessary to obtain the blue color.

**4. Hydrogen Iodide, HI.**—On a watch glass placed under the hood, add a few drops of  $12n \text{ H}_2\text{SO}_4$  to a few crystals of KI. The reactions are:



In the second reaction, is HI an oxidizing or a reducing agent?

Place 2 cc. test solution of KI in a test tube, add 5 drops  $6n \text{ H}_2\text{SO}_4$ , 1 cc.  $\text{KNO}_2$  solution and 1 cc. starch suspension. Dilute if the color is too dark, and warm gently if the color is slow in forming.

The reduction of  $\text{Fe}(\text{NO}_3)_3$  by HI can be shown by taking 2 cc. KI solution and adding 1 cc.  $6n \text{ HNO}_3$ , 2 cc.  $\text{Fe}(\text{NO}_3)_3$  solution and 2 cc.  $\text{CS}_2$ . Extract in a separatory funnel as you have previously done. Write the equations for the reactions.

### EXERCISES

1. Explain how the Nernst distribution coefficient can be applied to the extraction of  $\text{I}_2$  by  $\text{CS}_2$ .

2. Does the  $\text{CS}_2$  layer extract  $\text{Cl}_2$  as well as  $\text{I}_2$ ? Discuss the phases of this question in full.



3. Can the iodide-ion be completely displaced by means of chlorine water without removing the free  $I_2$  by a solvent? Explain.
4. Write a balanced equation for the reaction between  $H_2SO_4$  and  $HI$ .
5. What is the reaction between  $HI$  and water?
6. Explain in full the reaction in a solution containing  $KI$ ,  $H_2SO_4$ ,  $KNO_2$  and starch suspension.

### BROMIDE-ION, $Br^-$ (COLORLESS)

1. **Silver Bromide,  $AgBr$ .**—Precipitate  $AgBr$  from a solution of  $KBr$  by means of  $AgNO_3$ . Compare the characteristics of the precipitate with those of  $AgI$ . Test the solubility of the precipitate in  $NH_4OH$  as you did in the section on iodide-ion. Use comparable quantities throughout so that you can determine the relative solubilities of  $AgI$  and  $AgBr$  in  $NH_4OH$ .

2. **Displacement of Bromide-ion by Molecular Chlorine,  $Cl_2$ .**—Displace  $Br^-$  from a solution of  $KBr$  by means of chlorine water. Test the presence of free  $Br_2$  by extracting with  $CS_2$ . The color of  $Br_2$  in  $CS_2$  varies from a light yellow to a deep brown as shown in Plate V, *F* and *H*. The color of a bromine solution is not light and that of iodine dark, as many infer. The two colors are radically different.

Repeat the displacement of  $Br^-$  and extraction of  $Br_2$  by means of chlorine water,  $CS_2$  and the use of a separatory funnel, as you were directed to do for  $I_2$  in Paragraph 2 of the last section. Describe your results.

3. **Adsorption of Free Bromine by a Starch Suspension.**—Repeat Paragraph 3 of the last section, using  $KBr$  in place of  $KI$ . Will the starch suspension give a satisfactory test for iodine in the presence of bromine?

4. **Hydrogen Bromide,  $HBr$ .**—Add a few drops of 12*N*  $H_2SO_4$  to  $KBr$  crystals placed on a watch glass under the hood. Write the equations and compare the reducing action of  $HBr$  with that of  $HI$ . Which is the more unstable compound? What are the white fumes noticed above the watch glass?

Determine the reaction between a solution of  $KBr$ ,  $H_2SO_4$ ,  $KNO_2$  and a starch suspension. Point out any difference between this reaction and a similar one involving  $KI$ .

### EXERCISES

1. A bottle contains a saturated solution of  $Br_2$ . Make a list of the ionic and molecular species that are present.
2. Write an equation that will show the reaction between  $Br_2$  and  $K_2Cr_2O_7$ .



*Above.*—Laboratory of Bureau of Standards, Washington, D. C., in which samples of metals and alloys are analyzed.

*Below.*—Analysis of metals by electrodeposition in The Bureau of Standards.

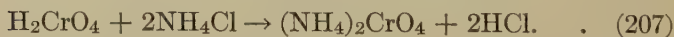
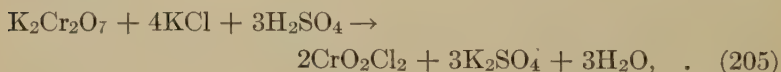
CHLORIDE-ION,  $\text{Cl}^-$  (COLORLESS)

**1. Silver Chloride,  $\text{AgCl}$ .**—Obtain a precipitate of  $\text{AgCl}$  by a reaction between  $\text{AgNO}_3$  and  $\text{KCl}$ . Describe its characteristics. Compare its solubility in  $\text{NH}_4\text{OH}$  with that of  $\text{AgI}$  and  $\text{AgBr}$ . When was  $\text{AgCl}$  used before in the identification of a radical?

**2. Hydrogen Chloride,  $\text{HCl}$ .**—Determine the stability or instability of  $\text{HCl}$  as you did for  $\text{HI}$  and  $\text{HBr}$ . Is  $\text{HCl}$  a good reducing agent?

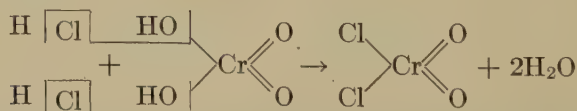
Determine the reaction between  $\text{KCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{KNO}_2$  and starch suspension. Can this reaction be used to determine the presence of a chloride?

**3. Chromyl Chloride,  $\text{CrO}_2\text{Cl}_2$ .**—Evaporate 3 cc.  $\text{KCl}$  test solution to dryness in an evaporating dish, scrape up the residue with a small piece of broken porcelain and add twice the volume of solid powdered  $\text{K}_2\text{Cr}_2\text{O}_7$ . Place this mixture in a small distilling tube and moisten with a few drops of  $18n$   $\text{H}_2\text{SO}_4$ . Distill into 2 cc.  $6n$   $\text{NH}_4\text{OH}$  containing 2 drops of  $\text{Ba}(\text{NO}_3)_2$  solution. The reactions are:

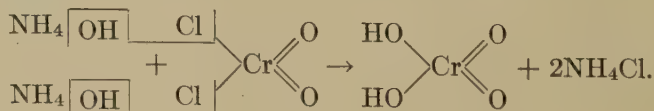


The presence of  $(\text{NH}_4)_2\text{CrO}_4$  gives a yellow solution, and, with a soluble salt of barium, yellow  $\text{BaCrO}_4$  is precipitated.

The reactions can be better understood by using structural formulas and noting the displacement of  $\text{OH}^-$  in chromic acid by  $\text{Cl}^-$  from  $\text{HCl}$ .



In the presence of water or a base, the  $\text{Cl}^-$  is replaced by  $\text{OH}^-$  as shown by



The  $\text{H}_2\text{CrO}_4$  reacts with  $\text{NH}_4\text{OH}$  by double decomposition, giving  $(\text{NH}_4)_2\text{CrO}_4$ , or, in the presence of  $\text{Ba}(\text{NO}_3)_2$ , the yellow precipitate of  $\text{BaCrO}_4$ .

Chromyl chloride is a reddish-brown liquid boiling at  $118^\circ$ . The corresponding compounds of bromine and iodine do not form, hence this is a good test for chlorides in the presence of the other halides. In making the chromyl chloride test it is evident that water cannot be present in the distilling tube or the  $\text{CrO}_2\text{Cl}_2$  will be decomposed, with  $\text{H}_2\text{CrO}_4$  and  $\text{HCl}$  resulting. When the  $\text{HCl}$  distills over into the  $\text{NH}_4\text{OH}$  solution,  $\text{NH}_4\text{Cl}$  is formed, and not a chromate. This distillation must be carried out slowly and carefully and continued long enough so that the air is displaced from the apparatus and the red liquid distills over. By using the bent-tube distilling apparatus, which has been described previously, there will be no danger of any liquid being drawn back into the hot distilling tube and causing a steam explosion.

#### EXERCISES

1. There is no paragraph on displacing the chloride-ion in this section. Why?
2. Will the starch test be of any value in determining the presence of  $\text{Cl}_2$ ?
3. In the chromyl chloride test, why does  $\text{Cl}^-$  replace  $\text{OH}^-$  in one case, and  $\text{OH}^-$  replace  $\text{Cl}^-$  in another?
4. Explain, by using the data obtained in these experiments, the difference between the displacing power of the halogens and their reducing power. For example, chlorine will displace iodine from a solution of an iodide, but  $\text{HI}$  is a better reducing agent than  $\text{HCl}$ .

#### FERRICYANIDE-ION, $[\text{Fe}(\text{CN})_6]^{-3}$ (COLORLESS)

**1. Silver Ferricyanide,  $\text{Ag}_3[\text{Fe}(\text{CN})_6]$ .**—Add 1 cc.  $\text{AgNO}_3$  reagent to 3 cc. test solution of potassium ferricyanide,  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . The orange-red precipitate is  $\text{Ag}_3[\text{Fe}(\text{CN})_6]$ . Filter and wash once with water. Test the solubility of parts of the precipitate in  $3n$   $\text{HNO}_3$  and  $6n$   $\text{NH}_4\text{OH}$ .

**2. Hydroferricyanic Acid,  $\text{H}_3[\text{Fe}(\text{CN})_6]$ .**—Take 1 cc. of a solution of  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , add 10 drops  $\text{HCl}$  and divide the solution into two parts. To one add a few drops of a solution of  $\text{FeSO}_4$  or  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ , and to the other, a few drops of  $\text{FeCl}_3$  solution. The first gives a deep blue precipitate of  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ , ferroferricyanide, or Turnbull's blue (see Plate II, O), and the second



gives a greenish-brown solution containing iron complexes of uncertain composition. Refer also to sections on ferrous-ion and ferric-ion in Part II. Which is the better test for the ferricyanide? Is any of the ferricyanide precipitate in colloidal suspension?

Take 1 cc. test solution of potassium ferricyanide solution, dilute with 5 cc. water and add a few drops of  $\text{NH}_4\text{SCN}$  solution. What does this show? Review the test of  $\text{Fe}^{+3}$  with  $\text{NH}_4\text{SCN}$ . Now add 10 drops  $12n$   $\text{HCl}$  and 3 cc. ether and shake the mixture. Allow to settle and explain the result.

### EXERCISES

1. Write the structural formula for hydroferricyanic acid and show all the valences. Do the same for ferrous ferricyanide.
2. Review the section on complex ions in Part I at this point in your work.
3. In Turnbull's blue is the color due to an ion or to a molecule?
4. If  $\text{H}_2\text{S}$  is passed through a slightly acid suspension of ferrous ferricyanide, what will be the result? Explain by means of equations.
5. What will be the relative concentration of hydrogen-ion in a solution of hydroferricyanic acid.
6. Will ferricyanides hydrolyze? Is a test solution of a ferricyanide made acid with  $\text{HCl}$ ?

### FERROCYANIDE-ION, $[\text{Fe}(\text{CN})_6]^{-4}$ (COLORLESS)

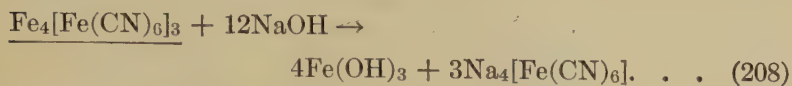
**1. Silver Ferrocyanide,  $\text{Ag}_4[\text{Fe}(\text{CN})_6]$ .**—Obtain this precipitate by using solutions of  $\text{AgNO}_3$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . Describe the color of the precipitate and test its solubility in  $3n$   $\text{HNO}_3$  and in  $6n$   $\text{NH}_4\text{OH}$ .

**2. Hydroferrocyanic Acid,  $\text{H}_4[\text{Fe}(\text{CN})_6]$ .**—Add a few drops of  $\text{HCl}$  to a test solution of potassium ferrocyanide. What is the color of the solution? To what is the color due? Divide the solution into two parts and test the first with a few drops of a ferric solution and the second with a few drops of a ferrous solution. The first gives a precipitate of ferric ferrocyanide, or Prussian blue (see Plate II, *P*), and the second gives a white precipitate of ferrous ferrocyanide which quickly changes to blue. Why? If you have difficulty in obtaining this white precipitate, refer to the section on ferrous-ion. Which is the better test for the ferrocyanide-ion?

Boil some of the Prussian blue precipitate with a solution of  $\text{NaOH}$ . Does the precipitate dissolve? Filter and wash. Test



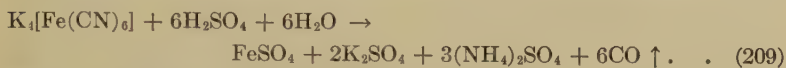
in the filtrate for the ferrocyanide radical. The reaction is shown by:



This is a good example of a reaction in which you start with one precipitate and end with another precipitate. In this case, the color of the precipitate changes, but there are other cases where both precipitates are of the same color. Always test in the filtrate to determine if solution has taken place.

### EXERCISES

1. The action of concentrated sulfuric acid on potassium ferrocyanide is shown by:



Show the electron balance in this equation.

2. Fusion with sodium carbonate will decompose ferricyanides and ferrocyanides. Explain the reaction and give the necessary equations.

### THIOCYANATE-ION, $\text{SCN}^-$ (COLORLESS)

1. **Silver Thiocyanate,  $\text{AgSCN}$ .**—Obtain  $\text{AgSCN}$  by the reaction of solutions of  $\text{AgNO}_3$  and  $\text{NH}_4\text{SCN}$ . Describe the precipitate and test the solubility in  $3n$   $\text{HNO}_3$  and  $6n$   $\text{NH}_4\text{OH}$ .

2. **Ferric Thiocyanate,  $\text{Fe}(\text{SCN})_3$ .**—Take 2 drops of  $\text{FeCl}_3$  solution and dilute with 20 cc. water, then add 2 drops  $\text{NH}_4\text{SCN}$  solution. Review the reaction in the section on ferric-ion. Warm the solution. Is the color removed? Add 4 drops  $\text{HgCl}_2$  solution to a solution that is not too deeply colored with the  $\text{NH}_4\text{SCN}$  molecule. What is the result? Add more  $\text{HgCl}_2$  or warm if necessary.

3. **Hydrothiocyanic Acid,  $\text{HSCN}$ .**—Place 2 cc. of test solutions of potassium thiocyanate, potassium ferricyanide and potassium ferrocyanide in the small bent-tube distilling apparatus. Add 2 cc.  $3n$   $\text{HCl}$  and 2 cc.  $\text{SnCl}_2$  solution. Distill into a test tube containing 3 cc. water and 5 drops  $6n$   $\text{HCl}$ . Divide the distillate into three parts and make separate tests for  $\text{SCN}^-$ ,  $[\text{Fe}(\text{CN})_6]^{-3}$  and  $[\text{Fe}(\text{CN})_6]^{-4}$ . What identification does this suggest?

## EXERCISES

1. What salts of HSCN are soluble?
2. Is HSCN present when a solution of  $\text{FeCl}_3$  and  $\text{NH}_4\text{SCN}$  are mixed, or is the reaction entirely one of double decomposition of two salts?
3. Is HSCN a strong acid? If  $\text{NH}_4\text{OH}$  is such a very weak base, how do you account for the possibility of the formation of a salt like  $(\text{NH}_4)_2\text{S}$  and  $\text{NH}_4\text{SCN}$ ?
4. What is the purpose of the stannous chloride in the distillation of HSCN?

SUMMARY OF REACTIONS OF THE ACIDS AND ACID RADICALS IN  
THE SILVER NITRATE GROUP THAT ARE OF IMPORTANCE IN  
ANALYTICAL PROCEDURE

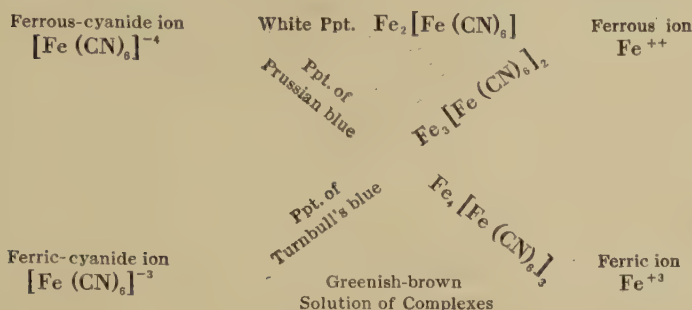
In making a review of the preliminary tests with the anions of the silver nitrate group, it is especially noticeable that the individual members have characteristic tests when alone. In the presence of other members of the group, however, there are several conflicts, some of which are difficult to overcome. For example, an iodide interferes with a test for a bromide, and both the iodide and the bromide interfere with the usual tests for a chloride. The bromide and iodide, especially the latter, interfere with the test for a thiocyanate, and the test is also obscured by the presence of ferricyanides or ferrocyanides. Finally, the presence of ferricyanides, ferrocyanides and thiocyanates may interfere with tests for the halides.

If one or two members of the group are present, a preliminary examination of the silver salts is worth while. They are as follows:

TABLE XIX  
SILVER SALTS OF GROUP III ANIONS

Acid Radical	Precipitate with $\text{AgNO}_3$	Characteristics of Precipitate
$\text{I}^-$ .....	$\text{AgI}$ .....	Light yellow, curdy.
$\text{Br}^-$ .....	$\text{AgBr}$ .....	Very light yellow, curdy.
$\text{Cl}^-$ .....	$\text{AgCl}$ .....	White, curdy.
$[\text{Fe}(\text{CN})_6]^{-3}$ ....	$\text{Ag}_3[\text{Fe}(\text{CN})_6]$ .	Orange-red, flocculent
$[\text{Fe}(\text{CN})_6]^{-4}$ ....	$\text{Ag}_4[\text{Fe}(\text{CN})_6]$ .	White, flocculent.
$\text{SCN}^-$ .....	$\text{AgSCN}$ .. . .	White, flocculent.

A summary of the tests of ferri- and ferrocyanides with iron radicals is of value.



The presence of  $\text{I}^-$  and  $\text{Br}^-$  can be determined by displacing with chlorine water and extracting with  $\text{CS}_2$ . Where these two radicals are absent, the test for  $\text{Cl}^-$  is readily accomplished by precipitating  $\text{AgCl}$  in a part of the prepared solution, and the rest of the identification consists in dissolving the precipitate in excess  $\text{NH}_4\text{OH}$  and reprecipitating with  $\text{HNO}_3$  as in the identification of  $\text{Ag}^+$  in metallic analysis. When  $\text{I}^-$  is present but no  $\text{Br}^-$ , it is possible to precipitate  $\text{AgCl}$  and  $\text{AgI}$  and then separate them by their difference in solubility in  $\text{NH}_4\text{OH}$ , but with both  $\text{I}^-$  and  $\text{Br}^-$  present there is a real problem in obtaining a satisfactory test for  $\text{Cl}^-$ .

We have seen that both  $\text{I}^-$  and  $\text{Br}^-$  can be displaced with chlorine water, but this method cannot be used where chlorides are to be determined later. Practically all methods of analysis remove iodides and bromides by making use of the greater instability of  $\text{HI}$  and  $\text{HBr}$  in the presence of oxidizing agents. Unless conditions are carefully controlled, however, the oxidation will also decompose  $\text{HCl}$ . The use of  $\text{K}_2\text{Cr}_2\text{O}_7$  in a moderately concentrated solution decomposes  $\text{HI}$  and  $\text{HBr}$  but will not decompose  $\text{HCl}$ , and this method is frequently used in procedures. The chromyl chloride test for a chloride will give uniform results if water is kept out of the distilling tube and the distillation is continued so long that chromyl chloride is actually distilled. If this test is carelessly performed, about all that passes into the distillate is  $\text{HCl}$  gas and water vapor.

The test for  $\text{SCN}^-$  cannot be made in the presence of an iodide, ferro- or ferricyanide. The iodide interferes by liberating  $\text{I}_2$

when  $\text{FeCl}_3$  is added, and this obscures the red of the  $\text{Fe}(\text{SCN})_3$  molecules. Ferro- and ferricyanides cannot be present because the addition of ferric-ion or ferrous-ion will give conflicting precipitates. By distilling some of the original solution made acid with  $\text{HCl}$  and containing an excess of  $\text{SnCl}_2$ , the  $\text{HSCN}$  will pass into the distillate where its identification is a simple matter. The presence of the  $\text{SnCl}_2$  prevents the decomposition of the halogen acids.

The ferro- and ferricyanides can be identified in separate portions of the Prepared Solution which has been made acid with  $\text{HCl}$  by adding ferric-ion and ferrous-ion.

Where ferro- and ferricyanides or thiocyanates are present they must be removed before making certain tests for the halides. The separation can be accomplished by precipitating the silver salts of Group III, filtering and washing. After separating the precipitate from the paper, it is ignited and the complex cyanides are decomposed, but the silver halides remain unchanged. The ignited residue is analyzed further, either by fusing with an alkali carbonate or by reducing with zinc and sulfuric acid.

#### PROCEDURE FOR THE ANALYSIS OF A PRACTICE SOLUTION CONTAINING ACID RADICALS OF GROUP III, THE SILVER NITRATE GROUP

The anions of Groups I and II are absent but there is no restriction placed upon the cations.

**Preliminary Tests.**—Take 2 cc. of the prepared solution, which is slightly acid with  $\text{HNO}_3$ , and add  $\text{AgNO}_3$  in excess. Carefully observe the color and other characteristics of the precipitate and draw conclusions by referring to the list of precipitates of silver salts in <sup>a</sup> Table XIX.

Make a second preliminary test by taking 1 cc. of the Prepared Solution, diluting with 2 cc. water and testing, in half-portions, for ferro- and ferricyanides by adding 3 drops  $\text{FeCl}_3$  and  $\text{FeSO}_4$  reagents, respectively. This test will also give some indication of the presence of iodides or thiocyanates. A red solution will indicate the presence of either substance.

**Identification of Iodides and Bromides.**—Take 2 cc. of the original solution, dilute with 2 cc. water, acidify with  $3n$   $\text{HCl}$  and add 2 cc. colorless  $\text{CS}_2$ . Now add  $\frac{1}{2}$  cc. chlorine water, shake for about ten seconds and allow to settle. A yellow or brown color-



**tion of the CS<sub>2</sub> layer** indicates bromides. A pink or red color indicates the presence of iodides, and this will necessitate an additional test to determine the presence of bromides. Place the entire contents of the test tube in a small separatory funnel and drain off the colored CS<sub>2</sub> layer from the bottom. Add another 2 cc. CS<sub>2</sub> and  $\frac{1}{2}$  cc. chlorine water to the residue in the funnel and extract and separate as before. Continue these extractions until all of the I<sup>-</sup> has been displaced and the I<sub>2</sub> removed by extraction. It is now possible to obtain a layer of CS<sub>2</sub> which is free from I<sub>2</sub> and one in which the characteristic **yellow or brown color of Br<sub>2</sub>** can be determined.<sup>b</sup>

**Identification of Thiocyanates.**—The thiocyanate-ion is next tested for, because we cannot continue with a test for a chloride in the presence of the CN complexes. The preliminary tests have already given information concerning the ferro- and ferricyanides. On the other hand, the presence of ferro- and ferricyanides and iodides interferes with SCN<sup>-</sup> determinations. If any of the three conflicting radicals are present, take 3 cc. of the original solution, add 1 cc. 6*n* HCl and 2 cc. SnCl<sub>2</sub> reagent. Place in the small bent-tube distilling apparatus and distill into 2 cc. of water containing 2 drops of FeCl<sub>3</sub> solution. The red color of **Fe(SCN)<sub>3</sub>** identifies thiocyanates.

If the conflicting radicals are not present, an identification of SCN<sup>-</sup> can be made during the preliminary tests with ferric-ion.<sup>c</sup>

**Identification of Chlorides.**—In the absence of all other members of this group, the test for a chloride can be made in the Prepared Solution by taking 2 cc. of the solution, adding 1 cc. 3*n* HNO<sub>3</sub> and precipitating with AgNO<sub>3</sub>. The precipitate of AgCl is filtered, washed once with water and dissolved by pouring 1 cc. 6*n* NH<sub>4</sub>OH over the filter. The filtrate is now neutralized with 6*n* HNO<sub>3</sub> and a curdy, white precipitate indicates the presence of **AgCl**, the test for a chloride.

In the presence of iodides or bromides, but with cyanide complexes absent, make the chromyl chloride test by taking 5 cc. of the original solution and evaporating to dryness. Scrape up the solid and add an equal volume of solid powdered K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, and mix thoroughly. Transfer to a bent-tube distilling apparatus and add 2 cc. 16*n* H<sub>2</sub>SO<sub>4</sub> and distill into 2 cc. 6*n* NH<sub>4</sub>OH containing a few drops of Ba(NO<sub>3</sub>)<sub>2</sub> solution.<sup>d</sup> A yellow precipitate of **BaCrO<sub>4</sub>** confirms the presence of a chloride.



When the cyanide complexes are present, take 10 cc. of original solution, add 1 cc.  $3n$   $\text{HNO}_3$  and precipitate with  $\text{AgNO}_3$  solution in excess. Filter, wash once with water and transfer precipitate to evaporating dish.<sup>6</sup> Evaporate to dryness and ignite. Cool after ignition and add about 1 gram of zinc and 2 cc. water.<sup>7</sup> Now add, dropwise,  $16n$   $\text{H}_2\text{SO}_4$  until there is a good evolution of gas. After one-half hour add 5 cc. water, bring to a boil and filter. Use the filtrate in tests for the halogen-ions.

#### NOTES ON THE PROCEDURE FOR THE ANALYSIS OF A PRACTICE SOLUTION CONTAINING GROUP III ANIONS

a. A white precipitate may contain  $\text{AgCl}$ ,  $\text{Ag}_4[\text{Fe}(\text{CN})_6]$  or  $\text{AgSCN}$ . If the precipitate is orange-red, then  $\text{Ag}_3[\text{Fe}(\text{CN})_6]$  is present, either alone or together with other members of the group. If the precipitate is only slightly colored, no definite information is imparted. A small amount of  $\text{Ag}_3[\text{Fe}(\text{CN})_6]$  with a white precipitate would not differ largely in color from a precipitate of  $\text{AgI}$  alone.

b. Unless the chlorine water is added in small portions, all of the  $\text{Br}_2$ , as well as the  $\text{I}_2$ , will be removed. With careful manipulation the  $\text{I}_2$  can be removed before the  $\text{Br}_2$ .

c. If a red color is obtained in the preliminary test when  $\text{FeCl}_3$  is the reagent, and subsequently no iodides are found to be present, then the red color was due to  $\text{Fe}(\text{SCN})_3$ .

d. Let it be emphasized again that the acid must be concentrated to avoid excess moisture in the tube and that distillation must be sufficiently prolonged.

e. Tear off excess filter paper and dislodge the precipitate by washing the paper in about 4 cc. water in the evaporating dish. Sometimes the filter paper is dried and the solid precipitate scraped from the surface.

f. This treatment reduces any iodates, bromates and chlorates that may have formed during the fusion. The subsequent treatment identifies  $\text{I}^-$  and not  $\text{IO}_3^-$ , etc.

#### OPTIONAL TESTS

Another method for the removal of the complex cyanides consists in igniting the precipitate of silver salts and then fusing with  $\text{NaKCO}_3$  and a small amount of  $\text{KNO}_3$ . The fused mass is extracted with water and reduced with  $\text{Zn}$  and  $\text{H}_2\text{SO}_4$  as previously described.

Ferro- and ferricyanides can be separated from other members of the group by making a prepared solution with  $\text{Na}_2\text{CO}_3$  and acidifying with  $\text{HAc}$  instead of  $\text{HNO}_3$ . Now, by adding a solution of  $\text{Ni}(\text{NO}_3)_2$  in excess, a precipitate of  $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$  and  $\text{Ni}_2[\text{Fe}(\text{CN})_6]$  will result and the solution will contain  $\text{NaSCN}$ ,  $\text{NaI}$ ,  $\text{NaBr}$  and  $\text{NaCl}$ .

A separation of particular value in the identification of chlorides can be continued from the last paragraph by taking the filtrate, adding 1 cc.  $3n$

$\text{HNO}_3$ , then  $\text{AgNO}_3$  in excess. Filter and wash once with water. Pour 5 cc. 15*n*  $\text{NH}_4\text{OH}$  over filter and pour solution back over precipitate one or more times, as long as further solution seems to be taking place. Some information concerning the character of the precipitate can be obtained when it is remembered that  $\text{AgCl}$  is completely soluble in  $\text{NH}_4\text{OH}$ , while  $\text{AgSCN}$  and  $\text{AgBr}$  are only sparingly so, and  $\text{AgI}$  is practically insoluble. Punch a hole in the bottom of the filter paper and wash the remaining precipitate down into a small evaporating dish by using the ammoniacal filtrate. Add, dropwise, colorless  $(\text{NH}_4)_2\text{S}$  reagent to the contents of the evaporating dish until no further precipitation takes place, then slowly boil for about one minute. Filter and discard precipitate of  $\text{Ag}_2\text{S}$  and again boil the solution until the odor of  $\text{NH}_3$  has disappeared. Refilter the solution if turbid. Add 1 cc. 6*n*  $\text{HNO}_3$ , 5 cc.  $\text{Fe}(\text{NO}_3)_3$  reagent and 2 cc.  $\text{CS}_2$ . Place in a separatory funnel. Shake and draw off  $\text{CS}_2$  layer. The red color of  $\text{I}_2$  in  $\text{CS}_2$  indicates iodides. Thiocyanates will color the water solution red. Continue extracting with  $\text{CS}_2$  until about colorless. Remove all traces of iodides by transferring contents of separatory funnel to an evaporating dish, bring to a boil for about two minutes, cool and add 1 cc. 6*n*  $\text{HNO}_3$  and a solution of  $\text{KMnO}_4$ , dropwise and with continued stirring, until the solution is permanently colored red. Now add 2 cc.  $\text{CS}_2$  and place in a separatory funnel and extract. The characteristic yellow or brown in the  $\text{CS}_2$  layer indicates bromides. Draw off the  $\text{CS}_2$  layer and discard. Transfer contents of funnel to a 200-cc. beaker and add 30 cc. water. Boil for seven minutes if bromides or thiocyanates are found to be present, and add more  $\text{KMnO}_4$  solution if boiling removes the characteristic red color. Disregard the formation of a brown precipitate of  $\text{Mn}(\text{OH})_3$  that may appear as the solution is boiled. Cool and add, dropwise and with constant stirring, a solution of  $\text{NaNO}_2$  until the precipitate, if any, has dissolved and the red color disappeared. Now add  $\text{AgNO}_3$  solution in excess; a precipitate of  $\text{AgCl}$  confirms the presence of chlorides.

## CHAPTER V

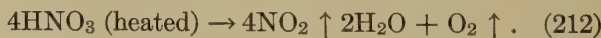
### GROUP IV.—THE SOLUBLE GROUP

#### NITRATE, $\text{NO}_3^-$

The soluble group consists of nitrates. Nitric acid and nitrates were not volatilized in Group I or subsequently precipitated by the group reagents  $\text{BaCl}_2$ – $\text{CaCl}_2$  and  $\text{AgNO}_3$ . Acetates are frequently placed in this group because their salts are quite uniformly soluble as with nitrates.

#### PRELIMINARY TESTS

1. **Nitric Acid,  $\text{HNO}_3$ .**—Take two test tubes and place in one 2 cc. test solution of  $\text{NaNO}_2$ , and in the other 2 cc. test solution of  $\text{NaNO}_3$ . Add, to each, 1 cc.  $3n \text{ H}_2\text{SO}_4$ . Is a gas evolved by either solution? Warm, but do not boil; note results. Cool both test tubes with tap water and add, to each, 1 cc.  $12n \text{ H}_2\text{SO}_4$ . Again carefully warm. These tests should clearly show the difference between the action of  $\text{HNO}_2$  and  $\text{HNO}_3$  in the presence of  $\text{H}_2\text{SO}_4$ . The decomposition of  $\text{HNO}_2$  takes place in cold dilute acids, while  $\text{HNO}_3$  requires stronger acids and frequent heating. The reactions for nitric acid are:

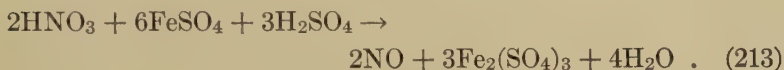


The decomposition of  $\text{HNO}_2$  is repeated for comparison:  $3\text{HNO}_2 \text{ (heated)} \rightarrow 2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O}$ ;  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \uparrow$ .

It will be observed that the reddish-brown fumes of  $\text{NO}_2$  are liberated in both decompositions. What is the physical state of  $\text{HNO}_3$  under ordinary conditions? Can tests for nitrates be made

in the presence of nitrites unless special procedures or reagents are used?

**2. Ferrous-nitrosyl Sulfate,  $\text{Fe} \cdot \text{NO} \cdot \text{SO}_4$ .**—This compound was made in the preliminary tests with nitrite-ion where it was shown that a nitrate is usually present as an oxidation product of a nitrite. Take 1 cc. test solution of  $\text{NaNO}_3$ , dilute with 2 cc. water, acidify with  $3n$   $\text{H}_2\text{SO}_4$  and add 5 drops of a solution of ferrous sulfate or ferrous ammonium sulfate. Hold the tube in an inclined position and carefully run down the inside of the tube, 2 cc.  $12n$   $\text{H}_2\text{SO}_4$ . At the junction of the two layers of liquid, the brown ring of  $\text{Fe} \cdot \text{NO} \cdot \text{SO}_4$  will be formed. The reactions are:



The ionization of ferrous-nitrosyl sulfate is shown by:



There are several substances that may interfere with the nitrate ring test. Add 1 cc. KI solution to a solution of a nitrate and make the ring test which was just described. Explain the interference. This represents one type of reaction that may interfere with a nitrate test. What other substances can be included in this type of interference?

Take a nitrate solution and add some  $\text{Pb}(\text{NO}_3)_2$  before making the ring test. What is the result? Mention other compounds whose presence will interfere in a similar manner.

Add some  $\text{K}_2\text{CrO}_4$  to a nitrate and then make the ring test. What constitutes the interference this time? Mention other similar interfering substances.

**3. Ammonium Nitrate,  $\text{NH}_4\text{NO}_3$ .**—Determine, as directed in the section on nitrites, whether the  $\text{NO}_3^-$  radical can be eliminated by adding a solution of  $\text{NH}_4\text{Cl}$  and then boiling.

### EXERCISES

1. Show the electron interchange in the equation where nitric acid is reduced by ferrous sulfate.

2. Will the gases coming from the decomposition of nitrates by  $\text{H}_2\text{SO}_4$  give a blue coloration with KI-starch paper? Explain in full.

SUMMARY OF REACTIONS OF NITRIC ACID AND THE NITRATE-ION  
THAT ARE OF IMPORTANCE IN ANALYTICAL PROCEDURE

The tests for a nitrate must be contrasted with those for a nitrite. We find that the nitrite is decomposed by weak acids, while a nitrate requires a concentration at least  $6n$  and warming. A brown gas, therefore, which results from a weakly acid solution and gives a blue color with KI-starch paper indicates a nitrite and not a nitrate.

The reducing action of a nitrite is in direct contrast to the characteristics of a nitrate.

The ring test for a nitrate cannot be made unless a nitrite is absent, because in this test a part of the nitrite is oxidized to a nitrate. There are also several substances that interfere with the ring test for a nitrate, among which are chromates, iodides, bromides, soluble salts of lead, silver, calcium, etc. In testing for a nitrate, the big problem is to remove the conflicting radicals or compounds.

The nitrate radical cannot be eliminated by boiling a solution of  $\text{NH}_4\text{NO}_3$ .

PROCEDURE FOR THE ANALYSIS OF A SOLUTION FOR A NITRATE

Since the analysis for the presence of a nitrate will come near the end in a systematic procedure, the many conflicting substances will have been determined. The characteristic ring test, giving  $\text{Fe} \cdot \text{NO} \cdot \text{SO}_4$ , is made in a portion of the original solution after the conflicting substances have been removed.

Where a nitrite is present, it can be removed by converting into ammonium nitrite, but, since there is always a part of it changed into a nitrate, the subsequent identification is of little value.

Iodides and bromides can be removed by acidifying the solution with  $3n$   $\text{H}_2\text{SO}_4$ . Now add a solution of  $\text{Ag}_2\text{SO}_4$  in excess and filter off the resulting  $\text{AgI}$  or  $\text{AgBr}$ .

When chromates are present, reduce with solid  $\text{Na}_2\text{CO}_3$  in a solution made acid with  $\text{H}_2\text{SO}_4$  and boil until a green color results. Remove the  $\text{Cr}^{+3}$  by making a Prepared Solution and removing the excess  $\text{Na}_2\text{CO}_3$  by acidifying with  $\text{H}_2\text{SO}_4$  and boiling.

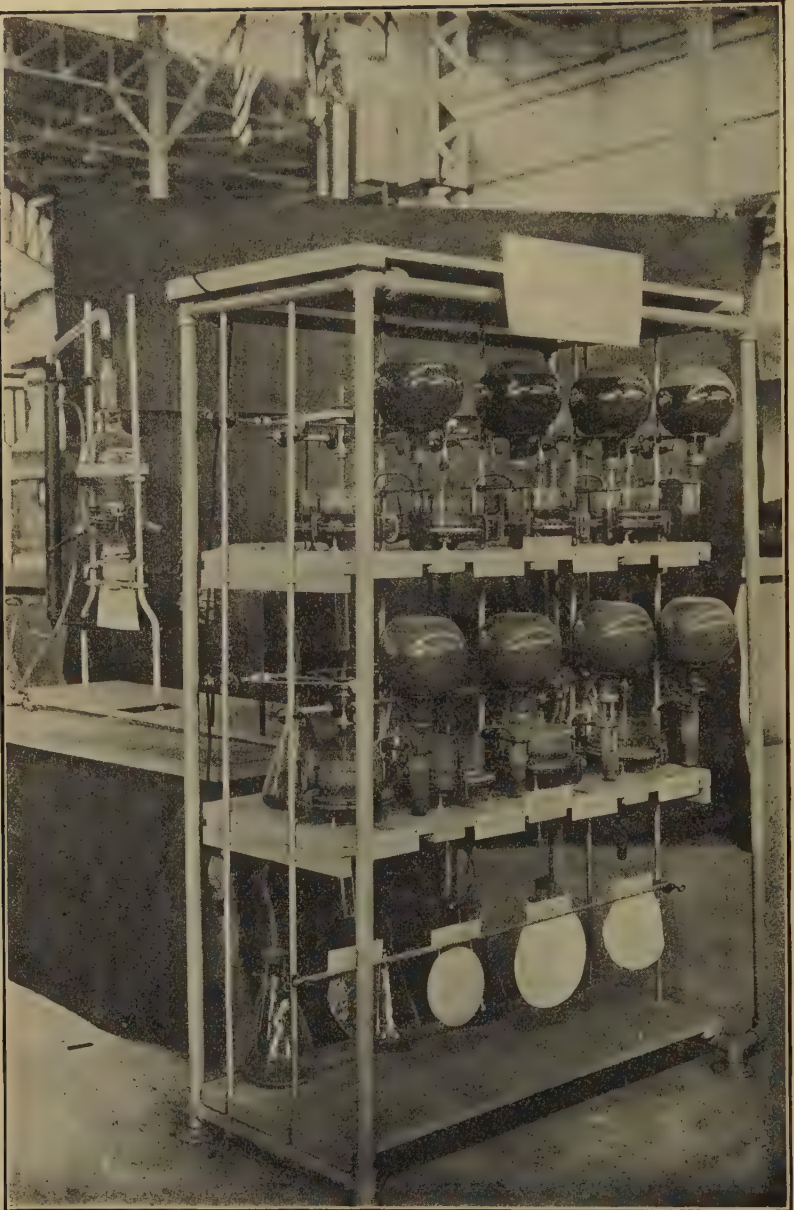
To remove ferro- and ferricyanides, add a few drops of  $\text{HCl}$  and



then precipitate with solutions of  $\text{FeCl}_3$  and  $\text{FeSO}_4$ . Filter and make the nitrate test in the filtrate.

Most of the conflicting substances will be removed in a systematic analysis by taking some of the filtrate from the  $\text{H}_2\text{S}$  group of metals and adding  $\text{Na}_2\text{CO}_3$ . After diluting with water and boiling, make the solution acid with  $\text{H}_2\text{SO}_4$  and boil to expel the volatile group of anions. Filter and add  $\text{Ag}_2\text{SO}_4$  to the solution in order to precipitate ferro- and ferricyanides, bromides and iodides. Filter and make the ring test in the filtrate.

The analysis of a solution for members of all groups of anions is not usually undertaken until the analysis of cations has been completed. The analysis is much simplified when the metallic radical content is known. Complete analysis for anions and cations is given in Part IV.



Apparatus for chemical separations may be very complicated. A special equipment is here shown for the determination of colloids. The United States Department of Agriculture, Bureau of Chemistry and Soils.

## PART IV

# COMPLETE ANALYSIS OF SOLUTIONS AND SOLIDS FOR CATIONS AND ANIONS

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### CHAPTER I

#### THE COMPLETE ANALYSIS OF SOLUTIONS

In Part II the analysis of a solution for cations was considered and in Part III there was presented a corresponding procedure for anions. In both procedures the analysis was limited to solutions, and it was also assumed that certain interfering substances, such as phosphates, tartrates, oxalates, etc. were absent.

We shall consider first in Part IV the question of interfering substances and their removal in the analysis of a solution, and then present a procedure for the complete analysis of a solution for cations and anions, with or without the presence of interfering substances. When the analysis of a solution has been completed, attention will be given next to the solution of a solid in preparation for analysis.

#### GENERAL CONSIDERATION OF INTERFERING SUBSTANCES

By referring to a solubility table in Part V it will be found that the majority of normal arsenates, arsenites, phosphates, oxalates, tartrates, silicates, borates and fluorides of all metallic radicals, except  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ , are quite insoluble in water but will dissolve in certain acids of moderate concentrations. These same substances are also quite insoluble in an alkaline solution.

When Groups I and II of cations are precipitated the solution is acid and the interfering radicals, therefore, remain in solution. When the filtrate from the  $\text{H}_2\text{S}$  group is made alkaline with  $\text{NH}_4\text{OH}$ ,

however, the conditions are favorable for the non-metallic interfering radicals to form insoluble compounds with any metallic radical present excepting  $K^+$ ,  $Na^+$  and  $NH_4^+$ . It should be recalled that arsenites and arsenates are to be removed by the reducing and precipitating action of  $H_2S$  in Group II and are not usually considered in the group of interfering radicals.

The composition and amount of precipitate which forms in the filtrate from the  $H_2S$  group when it is made alkaline and the interfering radicals are present depends upon the radicals that are present and the concentrations in which they occur. For example, suppose there is a relative excess of  $Fe^{+3}$ , very little  $Ba^{++}$ ,  $PO_4^{-3}$  and other non-metallic radicals. It is evident that the  $Fe^{+3}$  will remove all of the  $PO_4^{-3}$  as  $FePO_4$ . The solution will still contain  $Fe^{+3}$ ,  $Ba^{++}$  and non-metallic radicals. If the  $Fe^{+3}$  were limited, some  $Ba_3(PO_4)_2$  would also be precipitated, and with a large excess of  $PO_4^{-3}$  in the solution and very little  $Fe^{+3}$  and  $Ba^{++}$ , the metals would be completely precipitated and there would still remain in solution the excess of  $PO_4^{-3}$ . This, of course, is a very simple example but it will show the general nature of the problem which is presented by the presence of any of the interfering non-metallic radicals.

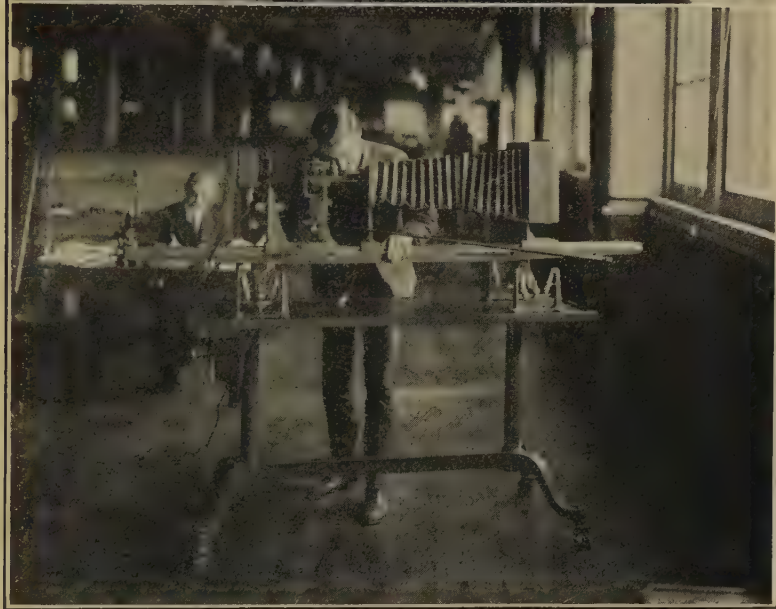
The preceding discussion has developed the fact that in the presence of certain interfering radicals the composition of Group III precipitate is very uncertain and may contain Group IV radicals and magnesium as well as those of Group III. The phosphate radical, therefore, is removed in a special procedure usually referred to as the **basic acetate separation**.

Another type of conflict is shown in the case of oxalates which frequently prevent the hydroxides and sulfides of Group III from separating as a compact precipitate, by developing a colloidal suspension. The removal of some of the interfering radicals will now be considered.

#### THE REMOVAL OF PHOSPHATE-ION

It has been pointed out that phosphates are soluble in acid solutions but it is necessary to qualify the statement at this time. The solubilities of phosphates can be arranged in terms of  $[H^+]$ , and it will be found that with a given concentration of hydrogen-ion the phosphate of iron is least soluble, while those of aluminum and chromium follow in the order given. The solubility of the





Two special analytical methods are shown in the research laboratories of the Bausch & Lomb Optical Company, Rochester, N. Y.

*Above.*—The concentration of a suspension is being determined by means of a “colorimeter.”

*Below.*—The analyst is making a study of a cross-section of an alloy. A photograph will be made later by means of the microphotographic apparatus.



phosphates of the remaining metals in Group III is much greater and the values are greatly increased in the alkaline-earth group and with magnesium. The phosphates of Groups I and II are very insoluble but they are not present in the filtrate which is used for Group III analysis. Presenting the facts another way: we can make the  $[H^+]$  of the solution for Group III of such a value that the phosphates of iron, aluminum and chromium will be practically insoluble.

There is another phase of the subject to be considered. If there is not a sufficient concentration of  $Fe^{+3}$ ,  $Al^{+3}$  and  $Cr^{+3}$  either as single radicals or as a combined concentration, then all of the  $PO_4^{-3}$  will not be removed and it will later precipitate metallic radicals when the solution is made alkaline.

The removal of the phosphate-ion will consist of an adjustment of  $[H^+]$  to make  $FePO_4$  insoluble; then we make certain that sufficient  $Fe^{+3}$  is present to remove all the  $PO_4^{-3}$ . The excess  $Fe^{+3}$ , over that necessary to precipitate the  $PO_4^{-3}$ , is removed by the formation of the precipitate,  $Fe(OH)_2C_2H_3O_2$ , basic ferric acetate. This method of removing the phosphate-ion is known as the basic acetate separation and refers to the method of removing the excess ferric-ion and not to the precipitate which actually removes the phosphate-ion.

**Procedure.**—After the filtrate from Group II has been boiled to remove the excess  $H_2S$  and then filtered to remove free S and any sulfides that may have passed through in colloidal suspension, take 3 cc. of the solution, add 2 drops 6*n*  $HNO_3$ , evaporate nearly to dryness, cool and add 2 cc. 3*n*  $HNO_3$ . Transfer to a test tube and add an equal volume of ammonium molybdate reagent<sup>a</sup> and warm gently, but do not boil, if no precipitate appears. The characteristic yellow precipitate of  $(NH_4)_3PO_4 \cdot 12MoO_3$  indicates the presence of phosphate-ion. If no phosphate is present, and since we are not concerned with other interfering radicals, the regular procedure for the analysis of Group III is followed. Where phosphate-ion is found to be present, add 3 drops 6*n*  $HNO_3$  to the entire filtrate and boil for about five minutes in a beaker. Transfer the solution to a 300-cc. flask and make a side test for ferric-ion.<sup>b</sup> Add  $NH_4OH$  dropwise<sup>c</sup> and with constant stirring until there is a permanent precipitate. Do not use the excess of  $NH_4OH$  that is usually necessary to obtain the maximum precipitate when Group III is precipitated.<sup>d</sup>

Now add  $3n$  HCl, dropwise, until the precipitate has dissolved to the extent that only a slight turbidity remains.<sup>e</sup> Dilute with 150 cc. water and add 15 cc.  $3n$   $\text{NH}_4\text{Ac}$  and 10 cc.  $6n$   $\text{HAc}$ .<sup>f</sup> If the solution is not a reddish-brown color due to an excess of  $\text{FeAc}_3$ ,<sup>g</sup> add  $\text{FeCl}_3$  or  $\text{Fe}(\text{NO}_3)_3$  solution, dropwise and with constant stirring, until the solution has a permanent red color.<sup>h</sup> Now boil for about five minutes,<sup>i</sup> cool, filter and wash once with water.

The precipitate contains  $\text{FePO}_4$  and  $\text{Fe}(\text{OH})_2\text{Ac}$  and may also contain  $\text{AlPO}_4$ <sup>j</sup> and  $\text{CrPO}_4$ .<sup>k</sup> In order to analyze the precipitate transfer it to an evaporating dish, add 2 cc. water and about  $\frac{1}{2}$  gram of solid  $\text{Na}_2\text{O}_2$ . After active effervescence has ceased, boil for about one minute, dilute with 10 cc. water and filter. The residue contains  $\text{Fe}(\text{OH})_3$ <sup>l</sup> and is discarded. The filtrate contains  $\text{Na}_3\text{PO}_4$  and the excess of  $\text{NaOH}$ ; it may also contain  $\text{Na}_3\text{AlO}_3$  or  $\text{Na}_2\text{CrO}_4$ . Make slightly acid with  $6n$   $\text{HNO}_3$ , add 2 cc.  $3n$   $\text{NH}_4\text{Cl}$  and make slightly ammoniacal. A white precipitate of  $\text{Al}(\text{OH})_3$  and  $\text{AlPO}_4$  indicates aluminum which can be confirmed by fusing with a few drops of a solution of  $\text{Co}(\text{NO}_3)_2$ . Chromium is identified in the filtrate with any method previously given in connection with chromium or the chromate ion.

The filtrate and washings from the phosphate precipitate contain an excess of  $\text{Fe}^{+3}$ , also  $\text{NH}_4\text{Ac}$  and acetic acid as well as other radicals of Group III and subsequent groups. If upon standing a further precipitate of  $\text{Fe}(\text{OH})_2\text{Ac}$  develops, add more water, boil, filter and discard the precipitate. To analyze the solution for the remaining metallic radicals, concentrate, cool, filter off any precipitate that forms and discard. Now add  $\text{NH}_4\text{Cl}$  and precipitate with  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{S}$ . Continue with Group III procedure.<sup>m</sup>

#### NOTES ON THE PROCEDURE FOR THE REMOVAL OF PHOSPHATE-ION

a. The test for a phosphate is made in the filtrate of the  $\text{H}_2\text{S}$  group and not in the original solution because arsenates must be absent when the test is made.

b. The test for iron before analyzing Group II might be unsatisfactory because of the formation of conflicting precipitates (see solubility tables for ferro- and ferricyanides). The test is made at this point so that iron can be reported and in order to determine whether a ferric compound must be added later in the basic acetate separation.

c. Notice that  $\text{NH}_4\text{Cl}$  is not added as it should be in the regular course of analysis of Group III. When  $\text{NH}_4\text{Ac}$  is added later, a high concentration of  $\text{NH}_4^+$  would reduce the concentration of  $\text{Ac}^-$  and this is not desirable.

d. A slight precipitate only is desired because it will be redissolved in the next step. If the precipitate is voluminous it may be necessary to use HCl or HNO<sub>3</sub> to dissolve it completely.

e. A slight turbidity is more desirable than an excess [H<sup>+</sup>], which is large enough to make the solution entirely clear.

f. A large [Ac<sup>-</sup>] is desired but not of [H<sup>+</sup>]. When HCl or HNO<sub>3</sub> is present in excess the concentration of acetate-ion is reduced. This is shown by the following ionization-constant ratio:

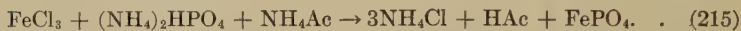
$$K_{\text{ion}} = \frac{\text{Total [H}^+ \text{]} \rightarrow \left[ \frac{[\text{H}^+]}{[\text{H}^+][\text{Ac}^-]} \right] \leftarrow \text{reduced concentration}}{\text{From HAc} \nearrow [\text{HAc}]}$$

NH<sub>4</sub>Ac must not be in large excess because the bivalent metals of Group III may also be precipitated.

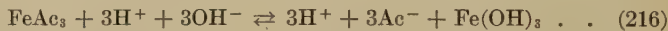
g. The dissolved molecules of FeAc<sub>3</sub> are red. There can also be present some colloidal Fe(OH)<sub>3</sub> which is a reddish-brown.

h. The color can be readily seen even in the presence of a precipitate. It is sometimes a yellow or amber. If the color is removed by boiling, add more ferric salt.

i. The reactions are:



Ferric hydroxide is also precipitated by the hydrolysis of ferric acetate as shown by:



j. Aluminum forms a precipitate of AlPO<sub>4</sub> but an excess of Al<sup>+</sup><sub>3</sub> will not be removed as a basic acetate unless the solution is kept hot. A basic aluminum acetate forms in the hot solution but redissolves when the solution is allowed to cool. This is one reason why Fe<sup>+</sup><sub>3</sub> is kept in large excess rather than Al<sup>+</sup><sub>3</sub>. Another reason is that an excess of FeCl<sub>3</sub> or FeAc<sub>3</sub> will color the solution and the excess will thereby be indicated, while the corresponding salts of aluminum are colorless.

k. If Fe<sup>+</sup><sub>3</sub> or Al<sup>+</sup><sub>3</sub> is in excess of Cr<sup>+</sup><sub>3</sub>, the latter can be precipitated as a basic acetate, but where Cr<sup>+</sup><sub>3</sub> is in excess the basic acetates are scarcely formed at all and most of the Fe<sup>+</sup><sub>3</sub> and Al<sup>+</sup><sub>3</sub> and all of Cr<sup>+</sup><sub>3</sub> will pass into the filtrate.

l. This procedure follows the method of metallic analysis as given in the optional tests when Group III consists of the hydroxides of iron, chromium and aluminum.

m. The filtrate may contain iron which, of course, is not reported on that basis alone. A test for chromium may be obtained in the basic acetate precipitate as well as in this filtrate. Remember to reserve the filtrate from the NH<sub>4</sub>OH-(NH<sub>4</sub>)<sub>2</sub>S precipitate for the analysis of Groups IV and V.

## PROCEDURE SHEET X

## PROCEDURE FOR THE REMOVAL OF PHOSPHATE-ION

## In the Absence of Oxalates, Tartrates and Other Organic Matter

Solution is the filtrate from Group II and has been boiled to remove  $\text{H}_2\text{S}$  and filtered if turbid.

Add 3 drops  $6n$   $\text{HNO}_3$ , boil for five minutes and transfer to 300-cc. flask.

Make side test for  $\text{Fe}^{+3}$  with  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

Add  $\text{NH}_4\text{OH}$  until slight permanent precipitate is obtained. Redissolve by adding dropwise  $3n$   $\text{HCl}$  until only a faint turbidity remains. Dilute with 150 cc. water, add 15 cc.  $3n$   $\text{NH}_4\text{Ac}$  and 10 cc.  $6n$   $\text{HAc}$ .

Add  $\text{FeCl}_3$  if solution is not red, and boil for five minutes. Cool, filter and wash precipitate once with water.

Precipitate:  $\text{FePO}_4$ ,  $\text{Fe}(\text{OH})_2\text{PO}_4$  and possibly  $\text{AlPO}_4$ ,  $\text{CrPO}_4$  and basic acetates of  $\text{Al}^{+3}$  and  $\text{Cr}^{+3}$ .

Transfer to evaporating dish, add 2 cc. water and  $\frac{1}{2}$  gram solid  $\text{Na}_2\text{O}_2$ . Boil, dilute, filter and wash once with water.

Residue:  $\text{Fe}(\text{OH})_3$  discard.  
Filtrate:  $\text{Na}_3\text{AlO}_3$ ,  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na}_3\text{PO}_4$  and excess  $\text{NaOH}$ . Add  $6n$   $\text{HNO}_3$  in slight excess, then 2 cc.  $3n$   $\text{NH}_4\text{Cl}$  and make alkaline with  $\text{NH}_4\text{OH}$ .

Precipitate:  
White ppt. of  $\text{Al}(\text{OH})_3$  and  $\text{AlPO}_4$ . Confirm if necessary.

Filtrate:  
 $\text{Na}_2\text{CrO}_4$ . Confirm by tests previously given.

Filtrate: Boil and refilter if turbid.  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$  and members of Groups IV and V may be present; also a possibility of  $\text{Cr}^{+3}$ . Analyze for metallic radicals from the beginning of Group III by adding  $\text{NH}_4\text{Cl}$  and precipitating with  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{S}$ , etc.

## THE REMOVAL OF OXALATE-ION AND ORGANIC MATTER

The presence of oxalates and organic matter may seriously interfere with the complete precipitation of Group III and with the formation of basic acetates. Where these substances are present the precipitates are usually kept in a colloidal suspension and cannot be coagulated as long as the interfering substances are present. We are considering the removal of oxalates and organic matter after the removal of phosphates because the procedure is usually



considered more difficult, and we are passing by a gradual development in procedure,<sup>a</sup> from the more simple analyses to those of considerable difficulty. Oxalates and organic matter are considered at the same time because they are removed by the same method.

**Identification of Oxalate-ion and Organic Material.**—Take 3 cc. of the filtrate from Group II, after the  $\text{H}_2\text{S}$  has been expelled and S filtered off. Make a Prepared Solution as you have previously done by adding an excess of  $\text{Na}_2\text{CO}_3$ , boiling and filtering. It may be necessary to dilute with water during the process. Remove the excess  $\text{Na}_2\text{CO}_3$  from the filtrate by adding concentrated  $\text{HAc}$  until acid and boiling.<sup>b</sup> Concentrate by boiling to 1 cc., cool and filter if necessary.<sup>c</sup> Test for acidity<sup>d</sup> and make acid with  $\text{HAc}$  if not distinctly so. Add an equal volume of saturated  $\text{CaSO}_4$ .<sup>e</sup> A white precipitate of  $\text{CaC}_2\text{O}_4$  insoluble in acetic acid indicates the presence of oxalates.

To test for organic matter, another 3-cc. portion of the filtrate from Group II, which has been freed of  $\text{H}_2\text{S}$  and S, is evaporated to dryness. Either transfer the solid to a closed tube<sup>f</sup> and heat to a dull red or heat in the evaporating dish. A **characteristic charring and odor**<sup>g</sup> indicates organic matter.

**Removal of Oxalates and Organic Matter.**—If the presence of oxalates or organic matter has been indicated, take the remaining filtrate from Group II and evaporate nearly to dryness<sup>h</sup> in an evaporating dish. Cool and add 7 cc.  $12n$   $\text{H}_2\text{SO}_4$  and warm and stir, but do not boil. Add more  $\text{H}_2\text{SO}_4$  if the mass seems to be thick and pasty. Now add 2 cc.  $12n$   $\text{HNO}_3$  and heat gently for one hour under the hood with stirring at intervals.<sup>i</sup> As the digestion with concentrated acids progresses, the charred mass decomposes and the liquid becomes a yellow or amber color. If sufficient decomposition<sup>j</sup> does not result from the first treatment, add 2 cc. each of  $12n$   $\text{H}_2\text{SO}_4$  and  $12n$   $\text{HNO}_3$  and continue the heating and stirring for another half-hour. Finally cool and pour the liquid into a beaker containing 40 cc. water, and boil for five minutes. Cool and filter and wash the solid matter on the filter with hot water. Oxalic acid has been decomposed into  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$ . Analyze the filtrate and washings for Group III and subsequent radicals except  $\text{Ba}^{++}$  and  $\text{Sr}^{++}$ .<sup>k</sup> The solid matter on the filter consists of the charred residue and may also contain  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ ,  $\text{CaSO}_4$ ,<sup>l</sup>  $\text{Cr}_2(\text{SO}_4)_3$  and  $\text{Fe}_2(\text{SO}_4)_3$ . Transfer the solids to an evaporating dish,<sup>m</sup> add 15 cc. water and 2 grams solid  $\text{Na}_2\text{CO}_3$ . Slowly digest



for one hour<sup>n</sup> and add water occasionally to keep volume constant. Dilute with 5 cc. water, filter and wash twice with cold water. Discard filtrate and washings. Dissolve the carbonates in the precipitate, which may consist of  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Cr}_2(\text{CO}_3)_3$ ,  $\text{Fe}_2(\text{CO}_3)_3$  and unconverted sulfates, by pouring 5 cc. hot 6*N* HAc over the filter one or more times.<sup>o</sup> Wash twice with hot water. This filtrate can be analyzed separately for Groups III and IV or combined with the original filtrate from the charred residue<sup>p</sup> and one analysis made for Groups III, IV and V.

#### NOTES ON THE REMOVAL OF OXALATE-ION AND ORGANIC MATTER

a. It is true that organic matter must be removed before the basic acetate separation can be made. It is also true that phosphates must be removed before Group III can be precipitated. No one would seriously consider the basic acetate separation before the study of Group III, and it is also unnecessary to consider the removal of organic matter before the removal of phosphates.

The removal of oxalates and organic matter is considered more difficult than the phosphate removal because the decomposition by concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  is often slow and incomplete and may result in losses of volatile matter. The alkaline-earth group is also precipitated as sulfates and this requires a subsequent fusion with  $\text{Na}_2\text{CO}_3$ . To separate the radicals from the charred mass requires at times a high degree of technical skill.

b. Recall that in metallic analysis we found that  $\text{CaC}_2\text{O}_4$  is insoluble in acetic acid but very soluble in a mineral acid.

c. Calcium oxalate is one of the precipitates that are difficult to obtain satisfactorily. The solution must be cool and concentrated and the precipitate may form slowly. It does not necessarily consist of crystals large enough to be seen by the naked eye unless slowly formed. A flocculent precipitate is more likely to result.

d. Boiling may have expelled most of the HAc.

e.  $\text{CaSO}_4$  is not very soluble and it is necessary to use a solution that is saturated. Make this reagent yourself and be sure that there is an excess of solid used in making the solution.

f. A "closed tube" is only closed at one end. In other words, it is a small test tube and can be made by taking a 4-inch length of glass tubing, heating in the center until plastic and then pulling the two halves apart. By heating the closed end in the flame it will be rounded off. Ignitions in a closed tube always give better results than in an evaporating dish because the escaping gases can be observed to better advantage and sublimates can be noted on the sides of the tube.

g. A dark residue does not necessarily indicate organic matter, because certain dark metallic oxides may be formed here. When concentrated sulfuric acid is added to the residue, a characteristic decomposition takes place and a black, frothy, charred mass results.

h. When evaporation is continued to dryness there is danger of losing substances by spattering, decomposition and volatilization.

i. An iron gauze with asbestos center is generally used. The flame can be increased until bubbles come from the liquid but it does not actively boil. Heating until  $\text{SO}_3$  fumes appear is unsatisfactory because they will frequently appear as soon as the liquid becomes hot. This has been discussed before when the precipitation of  $\text{PbSO}_4$  was considered. A slow decomposition with acid will accomplish more than using  $\text{H}_2\text{SO}_4$  of a concentration that may fume as soon as it becomes hot.

j. Additions of concentrated acids and repeated digestions must be continued until the charred mass is completely broken up and a yellow liquid results.

k.  $\text{BaSO}_4$  and  $\text{SrSO}_4$  are very insoluble and will be removed by this procedure, while  $\text{CaSO}_4$  has a much greater solubility. This will be evident from the following approximate solubilities in moles per liter of solution:  $\text{BaSO}_4$ , 0.041;  $\text{SrSO}_4$ , 0.036;  $\text{CaSO}_4$ , 0.015.

l. The residue was not washed with water until washings gave no further evidence of  $\text{SO}_4^{2-}$  (signifying  $\text{CaSO}_4$ ) because it is a slow process to dissolve completely, with water, a substance of solubility 0.015 from a mass of mixed salts. If the  $\text{CaSO}_4$  is retained as far as possible with  $\text{BaSO}_4$  and  $\text{SrSO}_4$ , its identification will be much simplified.

m. The transfer will probably be made by washing the paper in an evaporating dish with 15 cc. water and disengaging the solid matter by scraping. In this case another 15 cc. of water is not added. The black residue may obscure much of the sulfates which may also be present, so do not fail to make the tests which follow simply because you cannot see the white precipitate.

n. A large excess of  $\text{Na}_2\text{CO}_3$  and slow digestion over a considerable period of time are required. The reaction cannot be unduly hastened.

o. Acetic acid is used because the analysis in the presence of  $\text{Cr}^{+3}$  can proceed directly to that part of Group IV where the carbonates have been dissolved in acetic acid. The solution of the carbonate precipitate in HAc and not HCl or  $\text{HNO}_3$  was discussed in Group IV tests of metallic radicals. The presence of  $\text{Cr}^{+3}$  may be indicated by the green color of the solution but should be confirmed, when the solution is colorless, by the perchromic acid test. Have your instructor approve the method that you are going to use in making this test from this solution. If  $\text{CrAc}_3$  hydrolyzes in the acetic acid solution, add more acetic acid. If the precipitate will not redissolve, add a few drops of 12*N* HCl, but this addition must be considered in subsequent analysis. The phosphate-ion will not be in this solution.

p. The question of phosphate-ion is still to be determined. It will come down in this filtrate if present in the original solution and must be tested for and removed before Group III is continued. It is evident that an unknown containing a tartrate, a phosphate, no iron, but barium and magnesium, will give the analyst plenty to do,

## PROCEDURE SHEET XI

## PROCEDURE FOR THE REMOVAL OF OXALATES AND ORGANIC MATTER

Oxalates are identified by the formation of a white precipitate of  $\text{CaC}_2\text{O}_4$  in the filtrate from Group II metallic radicals. The presence of organic matter is shown by charring some of the same filtrate. Boil filtrate from Group II to remove  $\text{H}_2\text{S}$  and filter if turbid on account of S. Evaporate nearly to dryness, cool, add 7 cc. 12*n*  $\text{H}_2\text{SO}_4$ . Warm and stir and add more  $\text{H}_2\text{SO}_4$  if mass is too thick. Now add 2 cc. 12*n*  $\text{HNO}_3$ , heat for one hour under hood, and stir frequently. Add more  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  and reheat if decomposition is not complete. Cool, pour into 40 cc. water in beaker, boil five minutes. Cool, filter and wash with hot water. The oxalic acid has been eliminated as  $\text{CO}_2$ , CO and  $\text{H}_2\text{O}$ .

Residue and Precipitate: Charred carbonaceous matter, $\text{BaSO}_4$ , $\text{SrSO}_4$ , $\text{CaSO}_4$ , $\text{Cr}_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$ . Transfer to evaporating dish, add 15 cc. water, 2 grams solid $\text{Na}_2\text{CO}_3$ , digest for one hour, and during the digestion add water to keep constant volume. Dilute with 5 cc. water, filter and wash twice with cold water.	Filtrate: Groups III, IV, and V radicals except $\text{Ba}^{++}$ and $\text{Sr}^{++}$ . Analyze for Group III and subsequent groups. Also test for $\text{PO}_4^{-3}$ and make basic acetate separation if necessary before proceeding with Group III.
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Residue and Precipitate: Charred carbonaceous matter, $\text{BaCO}_3$ , $\text{SrCO}_3$ , $\text{CaCO}_3$ , $\text{Cr}_2(\text{CO}_3)_3$ $\text{Fe}_2(\text{CO}_3)_3$ . Dissolve in 5 cc. hot 6 <i>n</i> $\text{HAc}$ by pouring over filter one or more times. Wash twice with hot water.	Filtrate: Discard filtrate and washings.
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Residue: Charred carbonaceous matter. Discard.	Filtrate: $\text{BaAc}_2$ , $\text{SrAc}_2$ , $\text{CaAc}_2$ , $\text{CrAc}_3$ , $\text{FeAc}_3$ . Test for presence of $\text{Cr}^{+3}$ . If absent, analyze for Group IV radicals. If present analyze for Groups III and IV or combine with first filtrate obtained in this procedure which is then analyzed for Groups III, IV and V.	Note that $\text{BaAc}_2$ , $\text{SrAc}_2$ , $\text{CaAc}_2$ , $\text{CrAc}_3$ and $\text{FeAc}_3$ , can be combined with this filtrate for analysis.
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## THE REMOVAL OF ACETATES AND SILICATES

**Acetates.**—The presence of acetates causes a different type of conflict from that of oxalates, organic matter and phosphates. In the basic acetate separation of phosphates we have seen that

$\text{Fe}^{+3}$ ,  $\text{Cr}^{+3}$  and  $\text{Al}^{+3}$  form basic acetate compounds that are insoluble in alkaline solutions or in solutions which are acid with HAc. It follows, then, that if an acetate is present when the filtrate for Group III is made ammoniacal, basic acetates may result and a modification of the scheme of analysis will be necessary.

Acetates may also give hydrolysis products with certain metallic radicals in the original solution if there is not sufficient HCl or  $\text{HNO}_3$  present.

Acetates do not give a charred residue when heated, so that their presence must be determined by other methods which are outlined in the preliminary tests with acetate-ion in Part III. Acetates will be decomposed when the solution for the removal of oxalates is evaporated about to dryness with  $\text{H}_2\text{SO}_4$ .

**Silicates.**—If the original solution is alkaline, silicates may be present and silicic acid will be precipitated or put into colloidal suspension when the solution is made acid. An alkaline solution will not contain salts of  $\text{Hg}_2^{++}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{++}$  or most of the metallic radicals (see solubility table), so that the solution can be made acid with HCl without precipitating Group I or the insoluble chlorides. Any gelatinous precipitate that results when HCl is added can be filtered off and tested with the microcosmic bead. See page 255 for the removal of colloidal  $\text{H}_2\text{SiO}_3$  and the further analysis of the solution.

#### ANALYSIS OF A SOLUTION FOR ALL RADICALS THAT HAVE BEEN CONSIDERED

Details in this outline will be given only when the consideration of all cations, anions and the interfering radicals requires the procedure to be stressed at certain points. The detailed analyses of groups must be obtained from the procedure sheets and will be referred to as Sheet I, etc. Reference should be made frequently to the notes accompanying the procedure sheets.

**1. Preliminary Examination of the Solution.**—Make a preliminary examination of the solution according to the procedure for the complete analysis of cations on page 220.

**2. Preliminary Flame Tests and the Test for  $\text{NH}_4^+$ .**—Follow the procedure on page 221 and Sheet IX as far as it relates to these radicals.

**3. Analysis of an Alkaline Solution.**—If the solution is alkaline, the metallic radicals are limited and the possibilities can be seen



by referring to a solubility table. If a careful study is made of the bases and salts that can be present, it will be possible to analyze the solution by direct tests rather than by following a systematic procedure. A soluble silicate is one possibility and should be identified as follows:

Take 5 cc. of the solution and make acid with HCl. A white, gelatinous precipitate indicates silicic acid,  $\text{H}_2\text{SiO}_3$ . Filter and, if the filtrate contains the acid in a colloidal suspension, evaporate to dryness and dehydrate at  $120^\circ$  for one hour. Add 10 cc.  $3n$  HCl, digest for fifteen minutes and break up the mass with a glass rod. Filter and use the filtrate for further analysis. Test either precipitate for silicic acid by fusing with microcosmic salt. A turbidity of  $\text{SiO}_2$  indicates a silicate.

**4. Analysis of an Acid Solution for Cations, Group I.**—Take one-half of the sample for cation analysis and reserve the other half for the determination of anions. Mix the sample thoroughly before the division is made. Make a side test for Group I with a few drops which have been filtered if necessary. If Group I is present it is also desirable to make a side test for substances that will hydrolyze by dilution with water. Take 4 drops of the solution and add an equal volume of water. A turbidity indicates the presence of antimony, bismuth or tin, and Group I should be precipitated by adding  $3n$  HCl and not by diluting with water before precipitating. Follow the procedure on page 221 for the removal of any sediment and the analysis of the group.

**5. Analysis of Group II.**—After making preliminary tests for  $\text{Fe}^{++}$ ,  $\text{Fe}^{+3}$  and  $\text{Hg}^{++}$ , add the sediment, if any, which was removed before the precipitation of Group I. Make a side test for the presence of Group II by taking  $\frac{1}{2}$  cc. of the solution and the sediment, add 5 drops  $6n$  HCl and pass  $\text{H}_2\text{S}$  through. If Group II is not present, discard the side test and proceed to Group III. If the group is present add the side test to the main solution and follow Sheets II, III and IV for the precipitation and analysis of the group. Be sure to boil the filtrate and washings until  $\text{H}_2\text{S}$  is expelled, then cool and filter and reserve for Group III.

**6. Tests for Oxalates, Organic Matter and Phosphates, and Their Removal.**—Test for oxalates and organic matter by Sheet XI and if present continue the analysis of the solution as outlined in that procedure. Test for phosphates by Sheet X and if present continue the analysis as outlined.



**7. Test for Acetates and Their Removal.**—If oxalates or organic matter have been present, the elimination of acetates has also been accomplished during their removal. If phosphates are present, acetates will do no harm because in the basic acetate separation acetates are added to the solution.

In the absence of the above radicals a test should be made for acetates by evaporating some of the filtrate from Group II or 2 cc. of the original solution, nearly to dryness and making one of the tests outlined in the preliminary tests for acetates as given in the section on acetate-ion. If acetates are present they must be eliminated as described for oxalates in Sheet XI.

**8. Group III in the Absence of Interfering Substances.**—Where there are no interfering substances present, analyze the filtrate and washings from Group II by Sheets V, VI and VII. Concentrate filtrate and washings to 20 cc. Cool, filter if not clear, and proceed to Group IV.

**9. Group IV.**—Analyze according to Sheet VIII. As soon as the filtrate and washings are obtained, concentrate to 20 cc., cool, and add 2 cc.  $(\text{NH}_4)_2\text{SO}_4$  reagent and 2 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent. Shake thoroughly and set aside for at least two hours. This precipitation should be given as much time as possible, and standing over night is desirable. Filter through a double filter and proceed to the analysis of Group V.

**10. Group V.**—Proceed as outlined in Sheet IX. Do not make additional confirmatory tests for any of the metallic radicals until the analysis for non-metals has been completed. Special tests can then be made in the original solution for any radical whose presence seems to be doubtful.

**11. Anion Analysis, Preliminary Tests with  $\text{H}_2\text{SO}_4$ .**—Place 2 cc. of the original solution in a 3-inch test tube and add 1 cc.  $3n$   $\text{H}_2\text{SO}_4$ . The results and tests are summarized in the following table:

After the test with  $3n$   $\text{H}_2\text{SO}_4$  is completed, slowly add 1 cc.  $12n$   $\text{H}_2\text{SO}_4$  and warm gently. Do not boil. Charring will indicate a tartrate since there is no other organic substance included in the tests. Fuming when the breath is blown across the mouth of the tube, or in the presence of  $\text{NH}_4\text{OH}$ , usually indicates a halogen acid. Iodine from the decomposition of  $\text{HI}$  can be identified easily. In the absence of iodine vapor, the brown fumes of bromine can

TABLE XX

ACTION OF  $3n$   $\text{H}_2\text{SO}_4$  UPON A SOLUTION CONTAINING CERTAIN ACIDS

Gas Evolved	Identification	Acid
$\text{CO}_2$	Colorless. Gas escapes with active effervescence. Forms precipitate with lime-water film.	Carbonic
$\text{NO}$ and $\text{NO}_2$	$\text{NO}$ , colorless; $\text{NO}_2$ , brownish-red, $\text{NO}_2$ produces blue color on KI-starch paper.	Nitrous
$\text{SO}_2$	Colorless, characteristic pungent odor. Changes $\text{K}_2\text{CrO}_4$ paper to green.	Sulfurous
$\text{H}_2\text{S}$	Colorless, characteristic odor. Blackens lead acetate paper.	Hydrosulfuric
$\text{SO}_2$ , and S deposited in solution	Characteristics of $\text{SO}_2$ given under sulfurous acid.	Thiosulfuric or at least two of the following: Thiosulfuric, Sulfurous, Hydrosulfuric
$\text{CH}_3\text{COOH}$	Colorless, vinegar-like odor.	Acetic

be identified if  $\text{NO}_2$  is not still being eliminated by the decomposition of a nitrite or nitrate.

**12. Confirmatory Tests for Group I Anions.**—Make confirmatory tests as outlined in the procedure for Group I anions.

**13. Make a Prepared Solution** with 2 cc. of the original solution as described in the section on the Prepared Solution.

**14. Preliminary Tests with  $\text{AgNO}_3$ .**—Add 5 drops of  $6n$   $\text{HNO}_3$  to 3 cc. of the Prepared Solution and then an excess of  $\text{AgNO}_3$  reagent. A precipitate indicates the presence of Group III. Interpret the color of the precipitate of silver salts by referring to the list given in the summary of reactions in Group III. Filter off the precipitate and discard. Neutralize the filtrate with  $\text{NH}_4\text{OH}$  in slight excess. A precipitate indicates Group II. Interpret the color of the silver salts by referring to the summary of the reactions in Group II.

**15. Group II Anions, Confirmatory Test and Analysis.**—Follow outline as given in the procedure for the analysis of Group II anions.

**16. Group III Anions.**—Analyze according to procedure for Group III anions.

**17. Group IV Anions.**—Use the procedure for this group.

**18. Special Confirmatory Tests.**—With the results of analyses for both cations and anions before you, carefully check over the possibility of the combination being in a clear solution. Now is the time to make special confirmatory tests in the second half of the original solution when the first results are not entirely satisfactory. Plan reactions that will give you the identifications with the smallest number of operations. The radicals are reported in two groups, the cations and the anions.

## CHAPTER II

### THE COMPLETE ANALYSIS OF SOLIDS

In our analyses so far we have considered solutions only. In the analysis of solid material a preliminary examination is made and the color and general physical appearance of the sample is noted. Sometimes a careful study is made of the decomposition of the solid when heated in a closed tube and when dilute and concentrated sulfuric acid are added. The reaction of the solid when heated on a charcoal block with a blowpipe will often assist in the analysis, particularly if there are compounds of the heavy metals present.

In this course the time has been devoted very largely to analyses for radicals in solutions or, as it is termed, the wet method, so that when a solid is given for analysis the question of putting it into solution is of great importance. Many solids require special methods for solution and some of these will be considered in the succeeding sections on metals, alloys and silicates. A general consideration of the problem is next presented.

#### THE SOLUTION OF SOLIDS IN GENERAL

**Preliminary Examination.**—The method of dissolving a solid consists in treating the sample with water, cold and hot, and then, if complete solution does not result, trying successively dilute and concentrated hydrochloric acid, cold and hot, dilute and concentrated nitric acid, cold and hot, and finally aqua regia. Whatever does not dissolve in these solvents is known as the insoluble residue and is put into solution by a process of fusion.

The subsequent analysis of the solutions resulting from the successive treatment with the solvents is usually resolved into two types of procedure: first, each filtrate or extraction is separately analyzed; second, the filtrates are combined for a general analysis. The objection to the second method is that when the

separate filtrates are combined a precipitate may result and this would mean the undoing of a part of the work already performed. For example, suppose the solid is a mixture of non-metallic powders and that the water extraction removes  $\text{AgNO}_3$ . There is also a residue which dissolves next in  $\text{HCl}$ . Now if these two solutions are mixed it is evident that a precipitate of  $\text{AgCl}$  results. This example is a simple one and the possible complications resulting from mixing the extractions are readily apparent.

Before adding any solvent to the entire sample it is a good plan to try the action of the solvents on small amounts of the solid in separate tests. Suppose, for example, the solid contains certain salts of antimony or bismuth. When water is added, a precipitate of basic salts will result by hydrolysis. These hydrolysis compounds are frequently not very soluble when subsequently treated with acids and remain as residues until the final fusion of the insoluble residue is made. If, on the other hand, water had not been added to the antimony or bismuth salts but the first solvents applied had been  $\text{HCl}$  and  $\text{HNO}_3$ , this last complication would have been avoided.

To make the side tests with solvents, take about a twentieth of a gram (usually a few crystals or grains of solid), place in a small test tube and add 2 cc. water. Shake thoroughly and, if a solid remains, try warming. It is often difficult to determine a partial solution of the solid by a casual inspection, so, if solution is not apparent, carefully decant some of the liquid through a filter paper and carefully evaporate on a watch glass. The amounts of residue will indicate whether it will be worth while to put into solution completely by using water. If hydrolysis has resulted, boil the solution and, after settling, decant the liquid and test the solubility of the hydrolysis product in  $\text{HCl}$ . If not entirely dissolved, try  $\text{HNO}_3$ .

If water has had no reasonable solvent action it can be decanted and 2 cc. 6*n*  $\text{HCl}$  next added; otherwise start with another small portion of sample. Try successively warming the 6*n*  $\text{HCl}$  solution, adding 1 cc. 12*n*  $\text{HCl}$  and finally 1 cc. 12*n*  $\text{HNO}_3$  and warming. The final test with acids is made by taking another small sample and adding 1 cc. aqua regia and warming very slightly.

After the treatment with  $\text{HCl}$  or  $\text{HNO}_3$ , it is often advisable to decant the acid when a solid remains and add water and boil for a few moments. This subsequent treatment with water will be



very efficient if salts like  $\text{BaCl}_2$  or  $\text{Ba}(\text{NO}_3)_2$  have been formed. They are quite insoluble in strong acids but readily soluble in water.

During the preliminary tests with acids you should not lose sight of the fact that salts of the volatile and unstable group of acids will be decomposed, and some preliminary testing, therefore, can be done at the same time.

The preliminary tests have indicated which solvent or series of solvents it is best to use, and we shall now discuss the use of the solvents in detail.

**Extraction with Water.**—When a complete or partial solution with water has been shown in the preliminary tests and in the absence of hydrolysis complications, take 2–5 grams of the solid for analysis, place in a 200-cc. flask, add 40 cc. water and boil for five minutes. If solution is complete, proceed to the analysis of cations and anions. If there is a partial solution, filter and set the filtrate aside in a labeled and stoppered test tube.

**Extraction with Hydrochloric Acid.**—When a residue results from the water extraction, punch a hole in the bottom of the filter paper and wash the precipitate into a 200-cc. flask by means of 10 cc. 6*n* HCl. Be sure that all of the solid is removed from the paper, and if necessary remove the paper, tear off the unused edge and wash the paper in the solution by stirring with a glass rod. Remove the paper before proceeding further. Where a residue still remains, try warming for ten minutes with frequent stirring and finally boil for about two minutes.

Five cubic centimeters 12*n* HCl can now be added, and the solution stirred but not heated any further for another five minutes. Finally dilute with 30 cc. water. If the solid is completely dissolved, the solution is taken for analysis. If there is a residue, filter and set aside the filtrate in a labeled and stoppered test tube.

**Extraction with Nitric Acid.**—Wash the residue into a small flask with 10 cc. 6*n*  $\text{HNO}_3$  and warm for five minutes with frequent stirring. Add 5 cc. 12*n*  $\text{HNO}_3$  and warm for another five minutes. If there is no residue the solution is taken for analysis. In case a residue is still present do not filter but try extracting with aqua regia.

**Extraction with Aqua Regia.**—Where there is still a residue transfer the contents of the flask from the  $\text{HNO}_3$  extraction to an evaporating dish and concentrate under the hood by boiling to about 7 cc. Now add 6 cc. 12*n* HCl and 4 cc. 12*n*  $\text{HNO}_3$  and warm

## PLATE VI

### BEAD TESTS

**A.** The platinum wire is cleaned the same as when it is used for flame tests with the exception that the yellow of sodium can remain. A convenient method to obtain a small loop is to wind the end of the wire around a pencil point just back of the lead. This will give the maximum sized bead that can be retained by the loop.

**B.** The heated platinum wire is dipped into powdered borax and the "borax ball" heated in the upper oxidizing flame.

**C.** The heating must be continued until the bead is perfectly clear. Borax, sodium tetraborate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , when heated loses water and the resulting clear bead is essentially a combination of boric acid anhydride,  $\text{B}_2\text{O}_3$  and sodium metaborate,  $\text{NaBO}_2$ . The bead when strongly heated can dissolve many metallic oxides which frequently impart a characteristic color. The resulting compound when  $\text{CuO}$  is dissolved may be  $2\text{NaBO}_2 \cdot \text{Cu}(\text{BO}_2)_2$ .

**D.** The borax bead is sometimes formed as a small globule on the end of a straight wire. It is more readily removed in this form but the color is not as distinct as with the film when retained in the loop.

**E.\*** The sodium carbonate bead can be used for the manganese fusion instead of heating the mixture of  $\text{Na}_2\text{CO}_3$ ,  $\text{KClO}_3$  and  $\text{Mn}(\text{OH})_3$  on a porcelain crucible cover. The fused bead is here shown without the  $\text{Mn}(\text{OH})_3$  present to bring out the fact that it is opaque and not transparent like the borax bead.

**F.\*** This manganese fusion was made by mixing  $\text{Na}_2\text{CO}_3$ ,  $\text{KClO}_3$  and a small amount of  $\text{Mn}(\text{OH})_3$ , as described in A of Plate III. After a mass of the substances had been taken up by the loop it was coated with finely powdered  $\text{KClO}_3$ , thereby supplying an excess of oxidizing material. The crucible cover method will give better results when the amount of precipitate is small because the white background assists in the detection of traces of the green  $\text{Na}_2\text{MnO}_4$ .

**G.\*** An improperly heated  $\text{Na}_2\text{CO}_3$  bead is shown. Gray and black particles make a test unsatisfactory.

**H.\*** The amethyst or violet borax bead of manganese. Oxidizing flame has been used.

**I.\*** The greenish-blue borax bead of copper in the oxidizing flame.

**J.\*** Reddish-brown borax bead containing excess of copper and heated in the reducing flame.

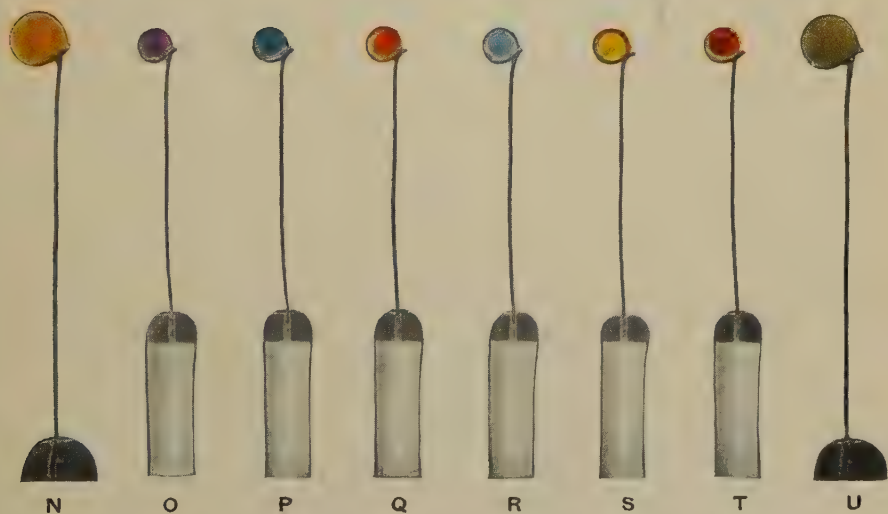
**K.\*** Blue borax bead of cobalt heated in the oxidizing flame.

**L.\*** Light greenish-blue borax bead of chromium heated in the oxidizing flame.

**M.\*** Dark reddish-brown borax bead of nickel heated in the oxidizing flame.

\* The beads marked with an asterisk have been enlarged  $2\frac{1}{2}$  diameters to show the color better. The other beads are natural size.

# PLATE VI





**N.\*** Yellowish-red borax bead of iron heated in the oxidizing flame. A large excess of iron is present.

**O.** Borax bead of Mn like **H** but natural size and used to give another variation in color.

**P.** Cobalt bead similar to **K**.

**Q.** Copper bead similar to **J**.

**R.** Chromium bead similar to **L**.

**S.** Borax bead of iron which is often a light yellow when hot and has been heated in the oxidizing flame. There is very little iron in this bead and when cold it is often colorless.

**T.** Nickel bead similar to **M**.

**U.\*** Iron borax bead heated in the reducing flame. The color is sometimes a brownish-green depending upon the concentration of iron, the salt used and the length of time of heating.



for ten minutes. Where there is still insoluble material, dilute with 20 cc. water and filter. Wash twice with water and reserve filtrate and washings for analysis. The insoluble residue is next considered.

**Examination of the Insoluble Residue.**—The procedure to be followed will be understood better if the possible composition of the insoluble residue is first examined. The following insoluble substances can be present either from the original solid or by reactions taking place during the digestion with acids:

(a) Insoluble lead salts as  $\text{PbCl}_2$  and  $\text{PbSO}_4$ .

(b) Insoluble silver salts as  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{AgSCN}$ ,  $\text{Ag}_3[\text{Fe}(\text{CN})_6]$  and  $\text{Ag}_4[\text{Fe}(\text{CN})_6]$ .

(c) Insoluble alkaline-earth sulfates as  $\text{BaSO}_4$ ,  $\text{SrSO}_4$  and  $\text{CaSO}_4$ .

(d) Insoluble oxides as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$  and  $\text{SiO}_2$  (or  $\text{H}_2\text{SiO}_3$ ).

(e) Insoluble complex silicates. Also C, S.

The insoluble residue is sometimes immediately fused with  $\text{Na}_2\text{CO}_3$ , but it is more satisfactory to remove as many of its components as possible by certain non-acid solvents before the fusion is finally made.

Transfer the residue to an evaporating dish and digest for one-half hour with 1 gram of solid  $\text{NH}_4\text{Ac}$  and 3 cc. 6*n*  $\text{HAc}$ . Stir frequently and warm very gently. Dilute with 5 cc. water, filter, wash once with water and test the filtrate for  $\text{Pb}^{++}$  and  $\text{SO}_4^{=}$ . The test for  $\text{Cl}^-$  is not made because this may result from the aqua regia as well as  $\text{PbCl}_2$ . Washing the residue until free of chloride-ion will also remove  $\text{PbCl}_2$ . If  $\text{PbCl}_2$  was present in the original solution it has been removed by the water extraction.

To test for silver salts, return to the residue on the filter paper and extract with 5 cc. 12*n*  $\text{NH}_4\text{OH}$  by pouring it over the solid a few times. Dilute the filtrate with 3 cc. water and neutralize with 12*n*  $\text{HNO}_3$ . Any precipitate resulting should be analyzed for  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{Ag}_3[\text{Fe}(\text{CN})_6]$  and  $\text{AgSCN}$ .

The presence of carbon is usually noticed by its color if it is not present in too small a proportion of the entire residue. Free sulfur is difficult to determine by casual inspection. A small amount of the residue carefully heated in a small closed tube will show the S as a sublimate on the wall of the tube.

Both C and S should be eliminated before the fusion is made.

Transfer the residue to a small evaporating dish and ignite until all S has been removed and the glowing particles of C have been oxidized to  $\text{CO}_2$ .

Carefully scrape up all of the residue and transfer to a small nickel or platinum crucible. Porcelain cannot be used because it may contaminate the fusion with radicals of silicates, calcium and aluminum. Make a fusion mixture of equal parts by weight of anhydrous  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$ , and add a few crystals of  $\text{KNO}_3$ . Thoroughly mix the residue with approximately five times its volume of the fusion mixture and heat strongly over a blast lamp or Meker type of burner until a clear melt is obtained. It may be necessary to add more of the fusion mixture during the heating.

After the fusion, cool the crucible, fill two-thirds full of hot water and allow to soak for one hour. The crucible can be very carefully warmed after the first ten minutes, and a glass rod should be used frequently to break up the fused mass and to assist in the water extraction. Finally filter and wash once with hot water.

Test for sulfates in the filtrate by first making slightly acid with  $\text{HCl}$  and then adding  $\text{BaCl}_2$  in excess.

The residue may consist of the alkaline-earth carbonates, metallic silver and silicates. Make a bead test for  $\text{SiO}_2$  with microcosmic salt and a few grains of the dried residue. Divide the rest of the residue into two parts. Extract the first part with  $6n$   $\text{HAc}$  to dissolve  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$ . Filter and test in the filtrate for the alkaline earth-radicals. Extract the second part with  $6n$   $\text{HNO}_3$  and test the filtrate for the presence of  $\text{AgNO}_3$ .

#### **Analysis of Solutions Resulting from Extraction with Acids.—**

Having disposed of the insoluble residue we shall now return to the extracted solutions which were previously stoppered, labeled and set aside. When the entire sample is water soluble, the analysis follows the regular procedure for the analysis of cations and anions. A preliminary test for acidic or basic properties of a water-soluble substance is very important because acidity can result from a limited number of solid acids or the solution of a non-metallic oxide, or by the hydrolysis of a salt which is made up of a weak metallic radical and a strong non-metallic radical. An alkaline solution, on the other hand, may be caused by the presence of a strong base, an oxide which forms a basic hydrate in solution or a salt which hydrolyzes and gives a basic solution.

When several filtrates have been obtained it is best to take a

few drops of each and put them together in a test tube and note whether a precipitate results. If there is precipitation, the filtrates must be analyzed separately. Where no precipitate results, a separate analysis can be made of each filtrate or a general one with the combined solutions.

In making an analysis of a strongly acid solution, difficulty is met with in the analysis of the  $\text{H}_2\text{S}$  group. On the other hand, it is sometimes a questionable procedure to evaporate nearly to dryness to remove the excess acid on account of the loss of volatile chlorides. When the solution for analysis results from the extraction with  $\text{HCl}$ , it can be diluted, before precipitating, with  $\text{H}_2\text{S}$ , to such an extent that the resulting acidity is  $0.3n$ . Then, after precipitation is complete, filter and evaporate the filtrate nearly to dryness and dilute with water, adding  $\text{HCl}$  to give a  $0.3n$   $\text{HCl}$  solution. The complete precipitation of the group can now be made and the precipitates combined for analysis.

When the residue is extracted with aqua regia the filtrate should be evaporated nearly to dryness to remove excess acid because the oxidizing action of the solution will have converted practically all of the volatile chlorides, especially those of arsenic, antimony and tin into oxides and oxygen acids.

In reporting the radicals determined in an analysis of a solid, it is very necessary to consider the additions that were made in the course of an analysis, as for example:



#### NOTES ON THE ANALYSIS OF SOLIDS

Although the procedure for the solution of a solid and the subsequent analysis of the various solutions contained much explanatory matter, the large number of possible combinations of solids in a sample makes it desirable to have the suggestions for analysis as complete as possible.

When a solid contains iodides or a mixture of iodine and potassium iodide there will be a continued interference from free iodine until it is practically all eliminated. Preliminary tests with acids, especially  $\text{H}_2\text{SO}_4$ , will indicate the presence of iodine or iodides by the evolution of the characteristic violet vapor. Add  $\text{HNO}_3$  to the solid and heat until no more iodine is liberated.

Sometimes  $\text{H}_2\text{SO}_4$  is used in the extraction of the solid after the water-soluble material has been removed. While this acid may be used in the solution of certain solids, its general use is not so good as that of  $\text{HCl}$  and  $\text{HNO}_3$ .

When  $\text{HCl}$  in not too great an excess is used as the extracting agent and

complete solution results, mercurous mercury, silver and large amounts of lead salts cannot be present. If a precipitate results when treating with  $12n$  HCl, it indicates the presence of Group I cations and can be filtered off and the solid tested for those ions. Whenever a precipitate forms during any acid treatment it can be filtered off and analyzed. The possible precipitates at various stages of the solution can be quite accurately determined by referring to solubility tables.

A gelatinous precipitate appearing during the digestion with HCl is probably silicic acid. Filter it off and, since it may contain metallic salts, dehydrate at  $120^\circ$  and extract with  $12n$   $\text{HNO}_3$ . Warm during the extraction and finally dilute with water and examine the precipitate for  $\text{SiO}_2$  and the filtrate for metals.

Most substances that are not soluble in water will dissolve in  $\text{HNO}_3$ , and for this reason it is selected as the most common solvent after water. By recalling the fact that the silver salts of Group II of anions are soluble in  $\text{HNO}_3$ , we see that the list may include arsenites, arsenates, borates, chromates, fluorides, oxalates, phosphates, sulfates, silicates and tartrates.  $\text{HNO}_3$  also dissolves most of the hydroxides, oxides and sulfides of the heavy metals as well as  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ . Oxides of Sn, Sb and Mn are not dissolved by  $\text{HNO}_3$  but are put into solution with HCl. Many compounds are oxidized by the action of  $\text{HNO}_3$ , especially those of  $\text{Hg}_2^{++}$ ,  $\text{As}^{+3}$ ,  $\text{Sb}^{+3}$ ,  $\text{Sn}^{++}$  and  $\text{Fe}^{++}$ . Sulfides are decomposed with the liberation of free S and the formation of some  $\text{SO}_4^-$ . The precipitation of the sulfates of  $\text{Ba}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ca}^{++}$  and  $\text{Pb}^{++}$  then follows.

The action of aqua regia may liberate S and bring about the precipitation of  $\text{AgCl}$ ,  $\text{PbCl}_2$ , and the sulfates of lead and the alkaline-earth metals.

The fusion with  $\text{Na}_2\text{CO}_3$  was explained in detail in connection with the identification for sulfates in the anion preliminary tests.

## SPECIAL ANALYSIS OF METALS AND NON-FERROUS ALLOYS<sup>1</sup>

**Preliminary Discussion.**—The analyses of metallic powders and alloys differ essentially from the types of analyses already considered in that they are chiefly soluble in acids, and that non-metals are almost entirely absent. The metals are confined to Groups I–III, with the possible exception of magnesium. The non-metals may be sulfur, arsenic, phosphorus and silicon.

Alloys result from the mixing of certain metals in a molten condition and subsequent cooling, and they may be either homo-

<sup>1</sup> The commercial varieties of iron and steel products require special procedures for satisfactory solution and analysis. The analysis of iron and steel is a highly specialized branch of analytical chemistry. Alloys containing gold and platinum are considered in a special section which immediately follows. The metals in this section are limited to those in Part II.



geneous or heterogeneous. One type of homogeneous alloy consists of metals which remain dissolved in one another even after cooling. The resulting solid is frequently referred to as a solid solution.<sup>2</sup> A second type of homogeneous alloy is in reality a supercooled liquid like glass and is non-crystalline. Frequently a crystalline structure will develop in the course of time. Alternate heating and cooling or vibration will promote the formation of crystals. In a third type of homogeneous alloy, compounds are formed of the metals present.

The average alloy may contain any combination of the three types just mentioned, as well as additional metals. In other words, an alloy is usually a solid of complex structure, and for this reason two samples of brass containing the same metals in the same amounts may present vastly different physical characteristics.

The solubility of alloys often presents striking differences. A part may dissolve very readily while the remainder even resists the solvent action of strong acids. If  $\text{HCl}$  is first added to an alloy, the members of Group I will be precipitated as an insoluble coating. When  $\text{HNO}_3$  is first used, oxides of antimony, tin and bismuth will form and these are insoluble in  $\text{HNO}_3$  but are soluble in  $\text{HCl}$ . These oxides will frequently entangle traces of metals and may also react with non-metallic groups, giving compounds such as tin arsenate, tin phosphate, etc. When very strong  $\text{HNO}_3$  is used (fuming nitric acid), certain metals become passive<sup>3</sup> and resist further attempts to put them into solution by ordinary methods. For this reason an alloy is never placed in contact with a strong acid at first. Sometimes an alloy is readily dissolved because a galvanic action is started when the metallic combination is placed in contact with the acid.

The following table gives the approximate composition of the more important alloys in common use.

<sup>2</sup> A solid solution consists of two or more substances that crystallize with the same fundamental pattern, or lattice, as it is termed. It has the characteristics of a liquid solution in that the amount of each component can be varied throughout a wide range.

<sup>3</sup> No satisfactory explanation has been given for the passive state. Iron, for example, having been in contact with fuming nitric acid, will not displace hydrogen from acids. Chromium and several other metals may develop this condition.



TABLE XXI

## APPROXIMATE COMPOSITION OF THE MORE COMMON NON-FERROUS ALLOYS

The less common substances that may be present are placed within parentheses. The number following the symbol represents approximate per cent.

Alloy	Composition
Amalgam.....	Hg and another metal
Babbitt's metal.....	Sn, 90; Sb, 7; Cu, 3
Bell metal.....	Cu, 75-80; Sn, 20-25
Brass.....	Cu, 60-82; Zn, 18-40; (Sn); (Pb)
Britannia metal.....	Sn, 90; Sb, 10
Bronze, ordinary.....	Cu, 81-86; Sn, 3-8; Zn, 11; (Pb)
, aluminum.....	Cu, 90-95; Al, 5-10
, silicon.....	Cu, 86-92; Sn, 8; Si, 1-6
, phosphor.....	Cu, 80; Sn, 10; Sb, 9; P, 1
, manganese.....	Cu, 95; Mn, 5
Dutch metal, artificial "gold leaf".....	Cu, 95; Zn, 5
German silver.....	Cu, 33-74; Zn, 20-45; Ni, 6-22
Gun metal.....	Cu, 90; Sn, 10
Manganin.....	Cu, 84; Mn, 12; Ni, 4
Nickel coins (U. S.).....	Cu, 75; Ni, 25
Pewter.....	Sn, 75; Pb, 25; (Cu); (Zn); (Sb)
Shot, hard lead.....	Pb, 99.5; As, 0.5
Solder, regular.....	Pb, 50; Sn, 50
, hard.....	Special brass or bronze
Type metal.....	Pb, 75-80; Sb, 20-25; (Ni); (Sn)
Wood's metal.....	Bi, 50; Pb, 25; Sn, 12.5; Cd, 12.5

**Solution of Metals and Non-ferrous Alloys.**—When the substance has been obtained from a machine shop it may be contaminated with oil. Thoroughly remove the oil by washing at least three times with naphtha or high test gasoline, and dry in the air in the absence of any flame. Place about 1 gram of a clean sample in an evaporating dish and add 10 cc. 6*n* HNO<sub>3</sub>. The solid should be as finely divided as possible and may consist of filings, turnings or drillings. Frequently stir the sample in contact with the acid, and after ten minutes warm gently and finally heat until NO<sub>2</sub> fumes are no longer given off. If a crystalline salt separates or if some of the original solid remains, add more acid and warm again. If all of the solid has dissolved, proceed to the analysis of the solution (solution A). Where there is a residue, decant the liquid (solution B) and reserve for final analysis. The residue may contain black carbon, gelatinous silicic acid, white oxides of anti-

mony, tin or bismuth, and particles of the original solid. If the action of the  $\text{HNO}_3$  has coated the original solid with white oxides, it is useless to continue the  $\text{HNO}_3$  treatment because the oxides of antimony, bismuth and tin are insoluble in  $\text{HNO}_3$  but will dissolve in  $\text{HCl}$ . In this case, wash the residue once by decantation and add 10 cc. 6*n*  $\text{HCl}$ . Heat for fifteen minutes or as long as solution appears to be taking place, but do not boil. If the solution is complete, add it (solution *C*) to solution *B* and analyze.

A residue may now consist of carbon, silicic acid, the chlorides of silver and lead and undissolved particles of the original solid. Add 5 cc. concentrated aqua regia and heat under the hood until the volume has been reduced one-half. Cool, add 5 cc. 6*n*  $\text{HCl}$  and filter. If there is no residue, add the solution (solution *C*) to filtrate *B* and analyze, otherwise filter and reserve filtrate (solution *D*) for final analysis.

**Analysis of Final Residue.**—Test for  $\text{Ag}^+$  and  $\text{Pb}^{++}$  in a part of the residue by Group I procedure. Dry the remainder of the residue and test a few grains for silicates by fusing with a  $\text{NaPO}_3$  bead. Place some of the solid in a closed tube and heat and identify *S* by the sublimate forming in the cooler end. Place the rest of the solid on a porcelain crucible cover and ignite. The glowing and final ignition of the dark residue proves the presence of carbon.

Sometimes the alloy disintegrates into white oxides when treated with nitric acid and does not remain as a solid with a white coating. A good method of handling this situation is to decant and wash, reserving the filtrate for the final analysis of solutions. The white residue can be treated with  $\text{Na}_2\text{S}_x$ , and the solution will consist of subdivision *B* of Group II of cations. Oxides of metals other than arsenic, antimony and tin will remain undissolved, and subsequent treatment with  $\text{HCl}$  and aqua regia may be necessary.

**Analysis of Solutions.**—To analyze solution *A*, evaporate nearly to dryness to expel the excess acid. Add 20 cc. water containing a few drops of  $\text{HNO}_3$  and analyze two-thirds of the solution for cations in Groups I–III and for *Mg*. In the remaining third, make tests for  $\text{SO}_4^{=}$ ,  $\text{PO}_4^{-3}$  and  $\text{AsO}_4^{-3}$ .

Solutions *B*, *C* and *D* can be analyzed separately as outlined for *A* or combined for analysis. If they are combined, a precipitate of Group I metals may result on account of being in solution in *B* and reacting with the  $\text{HCl}$  in *C*. In this case we consider that

Group I has been precipitated and then continue with the analysis.

When silicates are present in alloys in excess of 1 per cent, they may seriously interfere in the analysis of the solutions by remaining in part in colloidal suspension. They are removed by taking the solution which contains the gelatinous precipitate or the suspension of  $\text{H}_2\text{SiO}_3$ , evaporating to dryness at  $120^\circ$  and continuing to heat for one hour longer. Now add  $6n$   $\text{HNO}_3$  and thoroughly break up the mass with a glass rod. Filter and reserve filtrate for analysis.

**Interpretation of Results.**—The identification of metals will indicate their presence in the alloy but will give no information as to whether they were in the free state or in combination. A sulfate results from a sulfide or free sulfur, and a phosphate and an arsenate result from the oxidation of phosphorus and arsenic, respectively.

#### SPECIAL ANALYSIS OF AN ALLOY CONTAINING GOLD AND PLATINUM

Alloys that are used in dentistry may contain silver amalgams or various combinations of gold, platinum and silver. The method of analysis is quite similar to that of the non-ferrous alloys but additional tests are required for gold and platinum. The following procedure also considers the possibility of antimony and tin being present:

Place 0.1 gram of finely divided alloy in a small casserole and add 5 cc.  $12n$   $\text{HNO}_3$  and warm gently. Stir during the addition of the  $\text{HNO}_3$  and continue warming until the alloy is completely disintegrated or dissolved. If a sediment results it may contain tin or antimony as metastannic and antimonie acids as well as metallic particles of gold and platinum. Decant the liquid, wash by decantation and combine the two liquids. Dilute the combined solution with an equal volume of hot water and analyze the solution for metallic radicals according to the procedures already given.

When there is a white or gray sediment, add 5 cc.  $12n$   $\text{HCl}$  and digest for ten minutes. Now add an equal volume of boiling water and, after stirring, allow the solids to settle, decant and wash by decantation. The combined solution is to be analyzed for the presence of  $\text{SbCl}_5$  and  $\text{SnCl}_4$ . The residue may be dark gray or black instead of white, because of the presence of Au or Pt. In

this case, wash by decantation with two 3-cc. portions of 12*n* HCl. Now add 3 cc. 12*n* HCl and 1 cc. 12*n* HNO<sub>3</sub>, evaporate nearly to dryness, take up with 2 cc. 3*n* HNO<sub>3</sub> and divide into 2 portions in 2 test tubes.

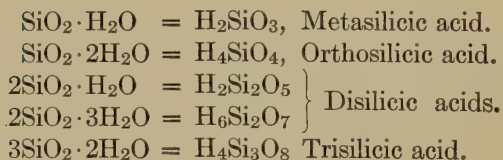
**Test for Gold.**—Dilute the first portion of liquid with 10 cc. water and add, dropwise, not over 10 drops of a test solution of SnCl<sub>2</sub> containing an equal volume of chlorine water. A purple or brownish-red color developing in the solution is due to the formation of a colloidal suspension of gold. When the suspension is purple, it is referred to as the "purple of Cassius."

**Test for Platinum.**—Add to the second portion of the solution 10 drops of a saturated solution of NH<sub>4</sub>Cl. A yellow precipitate of (NH<sub>4</sub>Cl)<sub>2</sub>·PtCl<sub>4</sub> identifies platinum. The precipitate may form only upon standing, and 5 drops of 95 per cent alcohol can be added to promote precipitation. When the amount of platinum is very small it may be necessary to evaporate to dryness over a hot water bath before the yellow crystalline precipitate of the double salt will be formed.

#### SPECIAL ANALYSIS OF SILICATES

In the section on non-ferrous alloys reference was made to the interference which silicates cause when present in amounts greater than approximately 1 per cent. When a silicate constitutes a large proportion of a solid it is necessary to use a special procedure for analysis.

The silicic acids result from various degrees of hydration of SiO<sub>2</sub>, and their inter-relation is shown in the following:



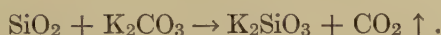
There are other members of the series, and when the possible salt combinations are considered it is evident that silicates as a class can be not only very numerous but complicated as well. Some of the common mineral silicates are:



Beryl.....	$\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ ,	Metasilicate
Talc.....	$\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ ,	Metasilicate
Garnet.....	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ ,	Orthosilicate
Kaolin.....	$\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$ ,	Orthosilicate
Mica.....	$\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$ ,	Orthosilicate
Serpentine (Asbestos).	$\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,	Disilicate
Orthoclase.....	$\text{KAlSi}_3\text{O}_8$ ,	Trisilicate

Besides the mineral silicates there are rocks that are made up in part of one or more silicates, as granite, which consists of quartz, feldspar and mica.

The alkali silicates, as  $\text{K}_2\text{SiO}_3$  and  $\text{Na}_2\text{SiO}_3$ , are the only ones soluble in water and are made by fusing  $\text{SiO}_2$  with an alkali carbonate:



This reaction is given because the complex silicates are put into solution by fusing with alkali carbonates and this reaction represents in a simplified form what occurs. Only the most elementary silicates are decomposed by  $\text{HCl}$  and  $\text{HNO}_3$ , and the tests for this type were given in the section on silicates in Part III. The mineral silicates require special fusions.

**Procedure.**—Mix 1 gram of finely pulverized sample with 2 grams each of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  and 1 gram of  $\text{KNO}_3$ . Place in a nickel or platinum crucible and heat over a Meker type burner or blast lamp until a clear melt is obtained. Cool, add 2 cc. water and 5 drops 12*n*  $\text{HCl}$ . After soaking for five minutes, warm very gently and transfer the contents of the crucible to an evaporating dish. Crush the solid with a glass rod and cover with 6*n*  $\text{HCl}$ . Evaporate to dryness and continue heating at about 120° in an air bath to render the silicic acid insoluble. Now add 5–10 cc. 6*n*  $\text{HCl}$  and stir at intervals with a glass rod for fifteen minutes. Dilute with 5 cc. water and filter. Test a small amount of the residue, which has been dried, for  $\text{SiO}_2$ , with the  $\text{NaPO}_3$  bead. The filtrate is analyzed for cations as given at the end of Part II or in the complete analysis of a solution, with the exception that the alkalies require a special procedure. This filtrate cannot be analyzed for  $\text{Na}^+$  and  $\text{K}^+$  because it has resulted from a fusion with sodium and potassium carbonates.



**Analysis for Alkalies.**—Place  $\frac{1}{2}$  gram of pulverized sample in a platinum crucible and thoroughly mix with 1 gram of alkali-free  $\text{NH}_4\text{Cl}$  and 7 grams of pure  $\text{CaCO}_3$ . Place the cover on the crucible and heat for forty-five minutes at a dull-red heat. Cool and extract with water and add 1 cc.  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  in excess to precipitate the excess  $\text{Ca}^{++}$ . Allow the precipitate to settle and filter through a double filter. Test the filtrate for  $\text{Na}^+$  and  $\text{K}^+$  as outlined in Part II.

## PART V

### OUTLINES OF COURSES AND THE MAINTENANCE OF A QUALITATIVE LABORATORY

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#### SUGGESTED COURSES IN QUALITATIVE ANALYSIS

This text has been planned so that it can be used for a two-semester one-year course or the shorter course which is completed in one semester.

**The Two-semester Course.**—The work is based upon two lecture or classroom hours and two laboratory periods of  $2\frac{1}{2}$ –3 hours a week with a make-up laboratory one afternoon every other week.

It is difficult to begin the laboratory work until a brief survey has been made of ionization, reversible reactions, the displacement of equilibria and the law of molecular concentration. It is therefore advisable to take the lecture hours and a part at least of the laboratory periods for the first two weeks of the course for a preliminary treatment of the most important parts of Chapters I–IV.

The laboratory work, beginning with the third week, will consist of the following:

1. Preliminary reactions showing the separation of cations into groups.
2. Preliminary reactions of Group I.
3. The analysis of a practice solution containing the radicals of Group I.
4. The analysis of an unknown on Group I.
5. Preliminary reactions of Group II.
6. The analysis of a practice solution containing the radicals of Group II.
7. The analysis of an unknown on Groups I and II.
8. The preliminary reactions of Group III.
9. The analysis of a practice solution containing the radicals of Group III.

10. The analysis of an unknown on Groups I-III.
11. Preliminary reactions of Group IV.
12. The analysis of a practice solution containing the radicals of Group IV.
13. The analysis of an unknown on Groups I-IV.
14. The preliminary reactions of Group V.
15. The analysis of a practice solution containing the radicals of Group V.
16. The analysis of an unknown on Groups I-V.
17. Preliminary reactions of the anions but not including oxalates, etc.
18. The analysis of a practice solution containing 3-5 metallic radicals which are posted on the board; the class is required to determine the non-metals only. This solution gives the first opportunity with anion analysis and therefore should not take any time for the determination of the cations.
19. The analysis of an unknown for both cations and anions but with interfering radicals absent.
20. The analysis of a practice solution involving the basic acetate separation. This solution can include 2-4 radicals of cation Groups I-II which are precipitated and discarded. Any radical of Group III can be present together with a soluble phosphate. It is also desirable to have some member of Group IV or V present, and this radical, together with that from Group III, should be determined so that the efficiency of the phosphate separation can be demonstrated.
21. The analysis of a complete unknown containing all possible cation and anion combinations, with the determination of the presence or absence of any of the interfering radicals.
22. The analysis of a solid unknown containing two or more salts.
23. The analysis of an unknown containing a mixture of metallic powders. This sample is easier to analyze than an alloy because it does not present the same difficulty of solution.
24. The analysis of one or more alloys or commercial products.

The lecture work after the first two weeks will continue with the chapters in Part I, and correlation will be made of the theoretical topics with the laboratory work. For example, the section on amphoteric hydroxides should be first considered or reviewed

in connection with the laboratory work on chromium, aluminum and zinc.

**The One-semester Course.**—The shorter course can be based upon this text by omitting the preliminary laboratory tests with the radicals. The summaries of reactions of the ions which immediately precede each scheme of analysis should be carefully reviewed. They will, to a limited extent, take the place of the preliminary work and will present the reasons for the steps followed in the procedures. The notes on each scheme of analysis are written in great detail so that they should be of special assistance to the one-semester student. The phosphates and other interfering radicals will probably have to be omitted, as will the analysis of alloys and commercial products. With these omissions the course can be covered in one term.

#### SOLUBILITY TABLES

Where a single substance is to be dissolved, reference to solubility tables is of great assistance. In these tables the solubilities of the common bases and salts are usually given in water, and in a few cases in hydrochloric acid, nitric acid and aqua regia.

In using solubility tables to determine the course of a reaction in analytical procedure it must be remembered that the ionization of a substance is very often greatly modified by the presence of other substances. For example, suppose we add 3 cc. of a certain reagent, AB to 5 cc. of a test solution of CD. We can calculate from the usual type of solubility table how much of AC will dissolve in 8 cc. of water, but after the reagent is added the solution may be acid or basic instead of neutral and this would require other tables to show the exact solubility of CD. In fact, if the solution is acid with HCl, we should know the amount of AC that will dissolve in HCl of the normality present in this 8 cc. of solution. If BD, the other product of the reaction, is not an acid but a salt, the solubility of AC will again have a different value and may be changed for every salt that can be present.

It must be emphasized that it is largely due to the impossibility of calculating the solubility of a substance in various solutions that the preliminary work in qualitative analysis is so important. In this laboratory work the solubility relationships are studied in sets

of preliminary experiments which are later duplicated as closely as possible in systematic procedures for analysis.

In obtaining values from solubility tables it must also be pointed out that the solubilities that are of the greatest importance to the analytical chemist are the ones that are the most inaccurately given. We are, of course, referring to the sparingly soluble salts. With very insoluble substances the analytical error in determining the solubility is often greater than the solubility of the substance itself, so that the result has little value. Again, when a sparingly soluble substance is put into solution by shaking an excess of the solid with a particular solvent for a long period of time, a part may result in true molecular solution and a part in colloidal suspension. By comparing the values given for the sparingly soluble sulfides in different tables, the truth of this last statement will become apparent.

We have already considered, on page 5, the solubilities of many substances in water, and on page 4 a series of solubility curves was presented to show the effect of temperature changes upon the solubility of certain substances in water. Two tables will now be given; the first is a general arrangement of certain groups according to their solubilities in water, and the second is a standard form of solubility table which is in quite general use.

TABLE XXII

GROUPS OF SALTS THAT ARE APPROXIMATELY SOLUBLE IN WATER, HYDROCHLORIC ACID, NITRIC ACID OR AQUA REGIA, AND THOSE THAT ARE PRACTICALLY INSOLUBLE. THE SALTS ARE IN THE SAME ORDER AS IN ANION ANALYSIS

## SALTS SOLUBLE IN WATER

**Carbonates.**—Those of the alkalies and the bicarbonates of Fe, Mn, Ba, Sr, Ca and Mg.

**Nitrites.**—All except  $\text{AgNO}_2$ .

**Sulfites.**—Those of the alkalies and the bisulfites of the alkaline earths.

**Sulfides.**—Those of the alkalies and alkaline earths except  $\text{CaS}$ .

**Thiosulfates.**—All except those of Ag and Ba.

**Acetates.**—All except those of Ag, Hg (ous), and certain basic acetates.

**Arsenites.**—Those of the alkalies.

**Arsenates.**—Those of the alkalies.

**Borates.**—Those of the alkalies.

**Chromates.**—Those of the alkalies, Cu, Mn, Fe, Zn, Sr, Ca and Mg.

**Fluorides.**—Those of the alkalies, Ag and Hg (ic).



TABLEX XII—*Continued*

**Oxalates.**—Those of the alkalies.

**Phosphates.**—Those of the alkalies (includes ortho, pyro and meta).

**Silicates.**—Those of the alkalies.

**Sulfates.**—All except those of Ba, Sr, Ca, Pb and certain basic salts.

**Tartrates.**—Those of the alkalies and the bitartrate of Na.

**Iodides.**—All except those of Ag, Hg (ous), Hg (ic), Cu (ous) and Pb.

**Bromides.**—All except those of Ag, Hg (ous), Cu (ous), BiOBr, SbOBr,

Mg<sub>2</sub>OBr<sub>2</sub> and Pb (sparingly in cold water but very soluble in hot water).

**Chlorides.**—Same as for bromides.

**Ferricyanides.**—Those of the alkalies and alkaline earths.

**Ferrocyanides.**—Same as for ferricyanides.

**Thiocyanates.**—Those of the alkalies, alkaline earths, Cu (ic), Hg (ic) and Fe.

**Nitrates.**—All except certain basic salts.

**Additional Salts.**—Molybdates, those of the alkalies; manganates and permanganates, all.

By inspecting the above lists it will be seen that salts of ammonium, potassium and sodium, as well as nitrates, nitrites (except AgNO<sub>2</sub>) and acetates (except AgAc and HgAc) are soluble in water.

## SALTS INSOLUBLE IN WATER, HYDROCHLORIC ACID OR NITRIC ACID

HgS, CaF<sub>2</sub>, PbSO<sub>4</sub>, BaSO<sub>4</sub>, SrSO<sub>4</sub>, AgCl, AgBr, AgI, Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>, SiO<sub>2</sub>, several silicates, C, fused PbCrO<sub>4</sub> and several oxides when strongly ignited, as SnO<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>.

## SALTS INSOLUBLE IN WATER, HYDROCHLORIC ACID AND NITRIC ACID BUT SOLUBLE IN AQUA REGIA

HgS and Sb<sub>2</sub>O<sub>3</sub>.

The majority of the remaining substances are put into solution by fusing with Na<sub>2</sub>CO<sub>3</sub> or KHSO<sub>4</sub> (except C and S) and extracting with water.

## TEST SOLUTIONS

The stock solutions are prepared with C.P. substances and distilled water. They contain 100 mg. per cc. of the essential radical unless the substance is insufficiently soluble; the concentration is then specially indicated.

The test solutions for students' use in the laboratory, unless otherwise specified, are made by taking 1 volume of stock solution and diluting with 9 volumes of distilled water. The resulting solutions, therefore, contain 10 mg. per cc.

Test solutions should not be used for reagent purposes and should be kept in a separate set of shelves.

TABLE  
OF

\* Taken from Wells' translation of the 16th

Showing the classes to which the compounds of the commonly occurring elements belong in respect to their solubility in water, hydrochloric acid, nitric acid or aqua regia.

## PRELIMINARY REMARKS

For the sake of brevity, the classes to which the compounds belong are expressed by letters. These have the following signification:

W or w, soluble in water.

A or a, insoluble in water, but soluble in hydrochloric acid, nitric acid, on in aqua regia.

I or i, insoluble in water, hydrochloric acid, or nitric acid.

Further, substances standing on the border lines are indicated as follows:

## SOLUBILITY

	Potassium	Sodium	Ammonium	Barium	Strontium	Calcium	Magnesium	Aluminum	Chromium	Zinc	Manganese	Nickel	Cobalt
Oxide.....	W	W	W	W	w	W-A	A	A	A&I	A	a <sub>17</sub>	A	A
Chromate.....	W <sub>1</sub>	w	w	a	w-a	w-a	.....	a	a	w	w	a	a
Sulfate.....	W <sub>13-15</sub>	W	W <sub>14-20-30</sub>	I	I	W-I	W	W <sub>13-14</sub>	W&I <sub>15</sub>	W	W	W	W
Phosphate.....	w	W <sub>3</sub>	W <sub>3-12</sub>	a	a	A <sub>11</sub>	a <sub>12</sub>	a	a	a	a	a	a
Borate.....	w <sub>2</sub>	w <sub>9</sub>	w	a	a	a	w-a	a	a	a	a	a	a
Oxalate.....	W <sub>3</sub>	W	W	a	a	A	a	a	w-a	a	w-a	a	a
Fluoride.....	w	w	W	w-a	w-a	A-I	a-1	w	w	w-a	a	w-a	w-a
Carbonate.....	W <sub>4</sub>	W <sub>10</sub>	W	A	A	A	A	.....	A	A	A	A	A
Silicate.....	w	W	.....	a	a	a	a	a-1	a	a	a	a	a
Chloride.....	W <sub>37</sub>	W	W <sub>21-38</sub>	W	W	W	W	W	W&I	W	W	W	W
Bromide.....	W	W	w	w	w	w	w	w	w&1	w	w	w	w
Iodide.....	W	w	W	w	w	w	w	w	w	w	w	w	w
Cyanide.....	W	w	w	w-a	w	w	w	.....	a	A	a	a-1	a-1
Ferrocyanide.....	W	w	w	w-a	w	w	w	.....	A-1	a	1	1	1
Ferricyanide.....	W	w	w	.....	.....	w	w	.....	a	1	1	1	1
Thiocyanate.....	W	w	W	w	w	w	w	.....	w	w	w	w	w
Sulfide.....	W	W	W	W	w	W-A <sub>45</sub>	a	a	a-1	A <sub>16</sub>	A	a <sub>13</sub>	a <sub>19</sub>
Nitrate.....	W	W	W	W	W	w	w	W	w	w	w	W	W
Chlorate.....	W	w	w	w	W	w	w	w	w	w	w	w	w
Tartrate.....	W <sub>5-6-7-22-46</sub>	W <sub>7</sub>	w <sub>6</sub>	a	a	A	w-a	w	w	a	w-a	a	w
Citrate.....	w	w	w	a	a	w-a	w	w	w	w-a	a	w	w
Malate.....	w	w	w	w&a	w	w-a <sub>47</sub>	w	w	.....	w	.....	.....	.....
Succinate.....	w	w	w	w-a	w-a	w	w	w-a	.....	w-a	w	w	w-a
Benzoate.....	w	w	w	w	w	.....	w	.....	.....	.....	.....	.....	.....
Salicylate.....	w	W	W	w-a	w-a	w-a	.....	.....	.....	.....	.....	.....	.....
Acetate.....	W	W	W	W	w	W	w	W	w	W	w	W	W
Formate.....	w	w	w	w	w	w	w	w	w	w	w	w	w
Arsenite.....	W	W	w	a	a	a	a	.....	.....	a	a	a	a
Arsenate.....	W	W	W	a	a	a	a	a	a	a	a	a	a

## NOTES TO TABLE OF SOLUBILITIES

1. Potassium dichromate, W. 2. Potassium borotartrate, W. 3. Hydrogen potassium oxalate, W. 4. Hydrogen potassium carbonate, W. 5. Hydrogen potassium tartrate, W. 6. Ammonium potassium tartrate, W. 7. Sodium potassium tartrate, W. 8. Ammonium sodium phosphate, W. 9. Acid sodium borate, W. 10. Hydrogen sodium carbonate, W. 11. Tricalcium phosphate, A. 12. Ammonium magnesium phosphate, A. 13. Potassium aluminum sulfate, W. 14. Ammonium aluminum sulfate, W. 15. Potassium chromium sulfate, W. 16. Zinc sulfide, as a sphalerite, soluble in nitric acid with separation of sulfur; in hydrochloric acid only upon heating. 17. Manganese dioxide, easily soluble in hydrochloric acid; insoluble in nitric acid. 18. Nickel sulfide is rather easily decomposed by nitric acid; very difficultly by hydrochloric acid. 19. Cobalt sulfide, like nickel sulfide. 20. Ammonium ferrous sulfate, W. 21. Ammonium ferric chloride, W. 22. Potassium ferric tartrate, W. 23. Silver sulfide, only soluble in nitric acid. 24. Minium is converted by hydrochloric acid into lead chloride; by nitric acid into soluble lead nitrate and brown lead peroxide which is insoluble in nitric acid. 25. Tribasic lead acetate, W. 26. Where a basic nitrate is also present, A. 27. Basic mercuric sulfate, A. 28. Mercuric amido-chloride, A. 29.

## XXIII

## SOLUBILITIES \*

German edition of Fresenius' *Qualitative Analysis*

W-A or w-a, difficultly soluble in water, but soluble in hydrochloric acid or nitric acid.

W-I or w-i, difficultly soluble in water, the solubility not being greatly increased by the addition of acids.

A-I or a-i, insoluble in water, difficultly soluble in acids.

If the behavior of a compound to hydrochloric and nitric acids is essentially different, this is stated in the notes.

Capital letters indicate common substances used in the arts and in medicine, while the small letters are used for those less commonly occurring.

The salts are generally considered as normal, but basic and acid salts, as well as double salts, in case they are important in medicine or in the arts, are referred to in the notes.

The small numbers in the table refer to notes given below.

TABLE

Ferrous	Ferric	Silver	Lead	Mercurous	Mercuric	Cupric	Bismuth	Cadmium	Gold	Platinum	Stannous	Stannic	Antimonious	
a	w	a	A <sub>34</sub>	A	A	A	a	a	...	a	a	a&l	A <sub>42</sub>	Oxide
...	w	A-I	A-I	a	w-a	w	a	a	...	a	a	a	a	Chromate
W <sub>20</sub>	W	W-A	A-I	w-a	W <sub>27</sub>	W <sub>30</sub>	w	W	...	w	w	a	w-a	Sulfate
a	a	a	a	a	a	a	a	a	...	...	a	a	...	Phosphate
a	a	a	a	a	...	a	a	W-a	...	...	a	...	...	Borate
a	a	a	a	a	...	a	a	a	...	w	a	w	a	Oxalate
w-a	w	w	a	...	w-a	a	w	W-a	...	...	w	w	w	Fluoride
A	a	a	a	a	a	a	a	a	...	...	...	...	...	Carbonate
a	a	...	a	...	...	...	a	a	...	...	...	...	...	Silicate
w	W <sub>21</sub>	I	W-I	A-I	W <sub>28</sub>	W	W-A <sub>33</sub>	W	W <sub>35</sub>	W <sub>37-33</sub>	W	W <sub>40</sub>	W-A <sub>43</sub>	Chloride
w	w	i	w-1	a-1	w	w	W-a	W	w	1	w	w	w-a	Bromide
W	w	i	W-A	A	A	w	a	a	W	w	...	...	...	Iodide
a-i	...	...	...	...	W	a	...	...	...	...	...	...	...	Cyanide
i	I	i	a	...	...	i	...	...	...	...	...	...	...	Ferrocyanide
I	w	i	w-a	...	...	...	...	...	...	...	...	...	...	Ferriocyanide
w	w	i	a	A	w	a	W-a	A	a <sub>36</sub>	a <sub>39</sub>	a <sub>41</sub>	a <sub>41</sub>	A <sub>44-45</sub>	Sulfide
A	a	a <sub>23</sub>	A	A <sub>29</sub>	a <sub>31</sub>	a	a	a	...	...	...	...	...	Nitrate
w	w	W	W	W <sub>26</sub>	W	W	W <sub>34</sub>	w	W	W	...	...	...	Chlorate
w	w	w	w	w	w	w	w	w	...	...	...	...	...	Tartrate
w-a	W <sub>22</sub>	a	a	w-a	a	w	a	W-a	...	...	a	...	a <sub>46</sub>	Citrate
w	W	a	a	w-a	w	w-a	w	...	...	...	...	w	...	Malate
...	W	w-a	w-a	a	w-a	w	...	...	...	...	...	a	...	Succinate
w-a	a	a	a	a	w-a	w	...	w	...	...	...	...	...	Benzoate
w	a	w-a	a	w-a	a	a	...	w	...	...	...	...	...	Salicylate
...	w-a	w-a	w-a	...	...	...	...	...	...	...	...	...	...	Acetate
w	W	w	W <sub>25</sub>	w-a	w	W <sub>32</sub>	w	w	...	...	w	w	...	Formate
w	W	w	w-a	w	w	w	w	w	...	...	...	...	...	Arsenite
a	a	a	a	a	a	A	...	...	...	...	...	...	a	Arsenate
a	a	a	a	a	a	a	a	...	...	...	...	a	a	...

Mercuric sulfide, not soluble in hydrochloric acid, nor in nitric acid, but soluble in *aqua regia* upon heating. 30. Ammonium cupric sulphate, W. 31. Copper sulfide is decomposed with difficulty by hydrochloric acid, but easily by nitric acid. 32. Basic cupric acetate, partially soluble in water, and completely in acids. 33. Basic bismuth chloride, A. 34. Basic bismuth nitrate, A. 35. Sodium auric chloride, W. 36. Gold sulfide is not dissolved by hydrochloric acid, nor by nitric acid, but it is dissolved by hot *aqua regia*. 37. Potassium chloroplatinate, W-I. 38. Ammonium chloroplatinate, dissolved by hot *aqua regia*. 39. Platinum sulfide is not attacked by hydrochloric acid, is but slightly attacked by nitric acid (if it has been precipitated hot), but is dissolved by hot *aqua regia*. 40. Ammonium stannic chloride, W. 41. Stannous sulfide and stannic sulfide are decomposed and dissolved by hot hydrochloric acid, and are converted by nitric acid into oxide, which is insoluble in an excess of nitric acid. Sublimed stannic sulfide is dissolved only by hot *aqua regia*. 42. Antimonious oxide, soluble in hydrochloric acid, not in nitric acid. 43. Basic antimonious chloride, A. 44. Antimony sulfide in hydrochloric acid, not in nitric acid. 45. Calcium antimony sulfide, W-A. 46. Potassium antimony tartrate, W. 47. Hydrogen calcium malate, W.

TABLE XXIV

COMPOSITION OF STOCK SOLUTIONS OF CATIONS AND ANIONS TO CONTAIN 100 MG. OF RADICAL PER CC. OF SOLUTION UNLESS OTHERWISE SPECIFIED. SOLUTIONS ARE CLASSIFIED ACCORDING TO THE GROUPS FOLLOWED IN SYSTEMATIC ANALYSIS

CATIONS			Grams per Liter of Solution
Group	Ion	Substance Dissolved	
I	Pb <sup>++</sup> .....	Pb(NO <sub>3</sub> ) <sub>2</sub> .....	159.8
I	Hg <sub>2</sub> <sup>++</sup> .....	Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O.....	139.9
Dissolve in 0.6 <i>n</i> HNO <sub>3</sub>			
I	Ag <sup>+</sup> .....	AgNO <sub>3</sub> .....	157.5
II	Hg <sup>++</sup> .....	HgCl <sub>2</sub> .....	67.6*
II	Bi <sup>+3</sup> .....	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O.....	231.6
Dissolve in 3 <i>n</i> HNO <sub>3</sub> .			
II	Cu <sup>++</sup> .....	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O.....	380.0
II	Cd <sup>++</sup> .....	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O.....	274.6
II	As <sup>+3</sup> .....	As <sub>2</sub> O <sub>3</sub> .....	13.2†
Digest with 500 cc. 12 <i>n</i> HCl and when dissolved dilute with water to 1 liter.			
II	As <sup>+5</sup> .....	As <sub>2</sub> O <sub>5</sub> .....	153.3
Dissolve by method for As <sub>2</sub> O <sub>3</sub> .			
II	Sb <sup>+3</sup> .....	SbCl <sub>3</sub> .....	186.0
Dissolve in 6 <i>n</i> HCl and dilute to 1 liter with 6 <i>n</i> HCl. Dilute with 2 <i>n</i> HCl in making a test solution from the stock bottle.			
II	Sn <sup>++</sup> .....	SnCl <sub>2</sub> ·2H <sub>2</sub> O.....	190.1
Dissolve in 6 <i>n</i> HCl.			
II	Sn <sup>+4</sup> .....	SnCl <sub>4</sub> ·3H <sub>2</sub> O.....	264.9
Dissolve the solid in 6 <i>n</i> HCl. If SnCl <sub>4</sub> liquid is used, take 219.5 grams.			
III	Co <sup>++</sup> .....	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O.....	494.2
III	Ni <sup>++</sup> .....	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O.....	493.7
III	Mn <sup>++</sup> .....	Mn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O.....	522.7
III	Fe <sup>++</sup> .....	FeCl <sub>2</sub> ·4H <sub>2</sub> O.....	356.0
Dissolve in <i>n</i> HCl. Keep C.P. iron wire in the solution.			
III	Fe <sup>+3</sup> .....	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O.....	723.5
III	Al <sup>+3</sup> .....	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O.....	695.0*
III	Cr <sup>+3</sup> .....	Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O.....	770.0
III	Zn <sup>++</sup> .....	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O.....	470.3
IV	Ba <sup>++</sup> .....	BaCl <sub>2</sub> ·2H <sub>2</sub> O.....	177.8

CATIONS—*Continued*

Group	Ion	Substance Dissolved	Grams per Liter of Solution
IV	$\text{Sr}^{++}$	$\text{Sr}(\text{NO}_3)_2$	241.6
IV	$\text{Ca}^{++}$	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	590.5
V	$\text{Mg}^{++}$	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	527.3*
V	$\text{K}^+$	$\text{KNO}_3$	258.6
V	$\text{Na}^+$	$\text{NaNO}_3$	369.6
V	$\text{NH}_4^+$	$\text{NH}_4\text{NO}_3$	445.0

## ANIONS

I	$\text{CO}_3^-$	$\text{Na}_2\text{CO}_3$	176.7
I	$\text{NO}_2^-$	$\text{NaNO}_2$	150.0
I	$\text{SO}_3^-$	$\text{Na}_2\text{SO}_3$	157.4
		$\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$	314.7
I	$\text{S}^-$	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	375.1*
I	$\text{S}_2\text{O}_3^-$	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	221.6
I	$\text{C}_2\text{H}_3\text{O}_2^-$	$\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$	230.5
II	$\text{AsO}_3^{-3}$	$\text{Na}_2\text{HAsO}_3$	138.2
II	$\text{AsO}_4^{-3}$	$\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$	152.6*
II	$\text{BO}_3^{-3}$	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	325.0*
II	$\text{CrO}_4^-$	$\text{K}_2\text{CrO}_4$	167.4
II	$\text{F}^-$	$\text{KF}$	305.8
II	$\text{C}_2\text{O}_4^-$	$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	209.1
II	$\text{PO}_4^{-3}$	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	188.5*
II	$\text{SiO}_3^-$	$\text{Na}_2\text{SiO}_3$	160.9
II	$\text{SO}_4^-$	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	335.6
II	$\text{C}_4\text{H}_4\text{O}_6^-$	$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$	155.5
III	$\text{I}^-$	$\text{KI}$	130.7
III	$\text{Br}^-$	$\text{KBr}$	148.7
III	$\text{Cl}^-$	$\text{NaCl}$	164.9
III	$[\text{Fe}(\text{CN})_6]^{-3}$	$\text{K}_3[\text{Fe}(\text{CN})_6]$	155.4
III	$[\text{Fe}(\text{CN})_6]^{-4}$	$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	199.4
III	$\text{SCN}^-$	$\text{KSCN}$	167.6
IV	$\text{NO}_3^-$	$\text{NaNO}_3$	137.1

\* Contains 50 mg. per cc. of solution. Dilute in the ratio of 1 cc. of solution with 4 cc. water to make test solution.

† Contains 10 mg. per cc. of solution.

## UNKNOWN SOLUTIONS

Great care must be exercised in making up unknown solutions. The soluble nitrates usually constitute the basis of the cation unknowns but the solutions will seldom contain equivalent amounts of the radicals present. For example, if a certain amount of lead nitrate and copper nitrate is first added to a stock bottle, the addi-





*Above.*—Mixers for standard samples of metals and alloys in The Bureau of Standards, Washington, D. C.; each mixer holds 1,000 pounds. In analytical procedure it is imperative that samples of a substance undergoing analysis be absolutely uniform.

*Below.*—Analytical laboratory of Eimer & Amend, New York City, in which analyses are being made for the purity of chemicals.

tion of a third nitrate may start the precipitation of the salt whose solubility product is first exceeded. This, of course, is not necessarily the one with the smallest solubility product because the concentration of the metallic radical, as well as the solubility product, is to be considered. The concentration of the nitrates can be decreased by dilution and then more of the third nitrate added, or a salt other than a nitrate can be taken for the third radical, provided, of course, that it does not form another precipitate with the radicals present.

This brief outline presents in a general way the essential problem in making up unknowns. The concentrations of radicals present should be carefully noted, however, so that the students' reports can be correctly judged.

When a large number of students are taking the course and twenty unknown solutions, for example, have been prepared for a certain group, the following method of filling the small bottles has proved very satisfactory and should eliminate any error in numbering the individual bottles:

First, number the small bottles consecutively and divide at random into twenty groups. Now place each group in front of a stock bottle and fill at one time from that stock bottle. Next copy down on the "Key Sheet" the numbers of the bottles containing each particular stock solution. Have another assistant check the numbers before the bottles have been removed from in front of the stock bottles. This method is far superior to arranging the small bottles consecutively and then filling certain ones from the stock bottle.

From the viewpoint of the student, all unknowns are more or less wrong unless he obtains a perfect analysis. He may report strontium, for example, when according to the key it is absent; and, furthermore, he can prove that it is present in his solution. All of which may be perfectly true, but it must be remembered that solutions are very easily contaminated. An uncleaned platinum wire may have been inserted in the solution, or the contents of the bottle when received from the instructor may have been poured into a flask that looked clean but was coated with an almost invisible glaze of metallic sulfides. In the preliminary discussion of laboratory procedure it was emphasized that glassware must be cleaned with acid at frequent intervals. Occasionally, however, there is a case where an error appears to have been made

in preparing the solution. The only method which will make it possible to check unknowns with certainty is to require each student to bring his own test tube or other container for the unknown solution. The instructor will then thoroughly mix the sample and give the student a two-thirds portion and reserve the one-third portion until the reports have been marked and returned to the students. The instructor by this method has an exact duplicate of the solution received by the student. This is, furthermore, the method of sampling which is usually followed in technical analyses and is the most satisfactory to both student and instructor.

### REAGENTS

Reagents should not be placed in the same section of shelves with test solutions.

### SOLUTIONS

#### ACIDS

**Acetic,  $\text{HC}_2\text{H}_3\text{O}_2$ .**— $6n$ ; dilute 350 cc. glacial acetic acid with water to 1 liter.

**Hydrochloric  $\text{HCl}$ .**— $6n$ ; mix the concentrated, sp.gr. = 1.19, with an equal volume of water.  $12n$ ; use the concentrated acid. This acid contains 37 per cent by weight of the gas  $\text{HCl}$ .

**Hydrochloroplatinic,  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ .**—10 per cent solution; dissolve 1 gram of the crystals in 9 cc. water. Keep in a dropping bottle.

**Hydrofluoric,  $\text{H}_2\text{F}_2$ .**—48 per cent solution; use the solution as purchased and keep in the special container.

**Nitric,  $\text{HNO}_3$ .**— $6n$ ; dilute 760 cc. of the concentrated, sp.gr. = 1.42, with water to 1 liter.  $16n$ ; use the concentrated acid as received.

**Perchloric,  $\text{HClO}_4$ .**—60 per cent; use the solution as purchased.

**Sulfuric,  $\text{H}_2\text{SO}_4$ .**— $6n$ ; dilute 155 cc. concentrated, sp. gr. = 1.84, with water to 1 liter. In diluting use an earthenware pitcher and pour the acid slowly into the water. Place the pitcher in running water to cool.  $12n$ ; dilute 310 cc. of concentrated acid with water to 1 liter.  $18n$ ; dilute 465 cc. concentrated acid with water to 1 liter. The concentrated acid contains 95 per cent  $\text{H}_2\text{SO}_4$  by weight.

**Tartaric,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ .**— $n$ ; dissolve 150 grams of the solid in water and dilute to 1 liter.

**Aqua Regia.**—Take 3 parts concentrated HCl and 1 part concentrated HNO<sub>3</sub>, and mix just before using.

## BASES

**Ammonium Hydroxide, NH<sub>4</sub>OH.**—6*n*; dilute 400 cc. of concentrated, sp.gr. = 0.90, with water to 1 liter. 15*n*; use the concentrated solution which contains 28 per cent by weight of NH<sub>3</sub>.

**Barium Hydroxide, Ba(OH)<sub>2</sub>.**—Saturated solution, "baryta-water," approximately 0.4 *n*; stir about 60 grams of solid Ba(OH)<sub>2</sub>·8H<sub>2</sub>O with 1 liter of water. Use a mechanical stirrer for one hour, or shake at intervals for two hours. Allow excess solid to settle and carefully decant supernatant liquid before use.

**Calcium Hydroxide, Ca(OH)<sub>2</sub>.**—Saturated solution, "lime-water," approximately 0.04 *n*; use about 10 grams of solid Ca(OH)<sub>2</sub> and prepare as with Ba(OH)<sub>2</sub>. The bottles containing baryta-water and limewater can be fitted with tubes containing soda-lime to exclude CO<sub>2</sub>.

**Potassium Hydroxide, KOH.**—6*n*; dissolve 336.6 grams of solid KOH in water and dilute to 1 liter.

**Sodium Hydroxide, NaOH.**—6*n*; dissolve 240 grams of solid NaOH in water and dilute to 1 liter.

## SALTS

**Ammonium Acetate, NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>.**—3*n*; dissolve 231.3 grams of the solid in water and dilute to 1 liter.

**Ammonium Carbonate, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O.**—3*n*; dissolve 171.1 grams of the hydrated or 144 grams of the anhydrous salt in water and dilute to 1 liter.

**Ammonium Chloride, NH<sub>4</sub>Cl.**—3*n*; dissolve 160.5 grams of the solid in water and dilute to 1 liter.

**Ammonium Molybdate, (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>.**—*n*; dissolve 88.3 grams of solid (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O in 100 cc. 6*n* NH<sub>4</sub>OH. Add 240 grams of solid NH<sub>4</sub>NO<sub>3</sub> and dilute with water to 1 liter. The solution can be prepared from MoO<sub>3</sub> by taking 72 grams of the solid and adding 130 cc. water and 75 cc. 15*n* NH<sub>4</sub>OH. Stir mechanically until practically all of the solid has dissolved, then add it to a solution of 240 cc. concentrated HNO<sub>3</sub> and 500 cc. water. Stir continually while the solutions are being mixed. Let stand for three days and filter and use the clear filtrate.



**Ammonium Nitrate,  $\text{NH}_4\text{NO}_3$ .**— $n$ ; dissolve 80.1 grams of the solid in water and dilute to 1 liter.

**Ammonium Monosulfide, "Colorless Ammonium Sulfide,"  $(\text{NH}_4)_2\text{S}$ .**—Approximately saturated; place 200 cc. concentrated  $\text{NH}_4\text{OH}$  in a flask set in cold water. Slowly pass  $\text{H}_2\text{S}$  through until the gas is no longer dissolved, then add 200 cc. concentrated  $\text{NH}_4\text{OH}$  and dilute with water to 1 liter.

**Ammonium Polysulfide, Yellow Ammonium Sulfide,  $(\text{NH}_4)_2\text{S}_x$ .** Approximately saturated; add 15 grams of sulfur to 200 cc. concentrated  $\text{NH}_4\text{OH}$  in a flask and saturate with  $\text{H}_2\text{S}$ . Now add 200 cc. concentrated  $\text{NH}_4\text{OH}$  and allow to stand for two days in the flask which has been stoppered. Finally dilute with water to 1 liter. Decant the supernatant liquid for use. Many prefer, however, to use the polysulfide with some suspended sulfur present.

**Ammonium Sulfate,  $(\text{NH}_4)_2\text{SO}_4$ .**— $n$ ; dissolve 132.2 grams of the solid in water and dilute to 1 liter.

**Barium Chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .**— $n$ ; dissolve 122.1 grams of the solid in water and dilute to 1 liter.

**Calcium Chloride,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ .**— $n$ ; dissolve 109.5 grams of the solid in water and dilute to 1 liter.

**Calcium Sulfate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .**—Saturated solution, approximately  $0.03n$ ; saturate a solution by mechanically stirring for at least three hours, 10 grams of the finely divided solid in a liter of water. Allow to settle and decant the clear liquid for use.

**Ferric Chloride,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ .**— $n$ ; dissolve 90.1 grams in 700 cc. water which contains 20 cc.  $12n$   $\text{HCl}$  or its equivalent in another concentration. Slowly dilute with water acidified with  $\text{HCl}$ , to 1 liter.

**Ferrous Sulfate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .**— $n$ ; dissolve 139 grams of the solid in water and dilute to 1 liter.

**Ferrous Ammonium Sulfate, Mohr's Salt,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ .**— $n$ ; dissolve 196.1 grams of the solid in water and dilute to 1 liter.

**Lead Acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ .**— $n$ ; dissolve 189.6 grams of the solid in water and dilute to 1 liter.

**Mercuric Chloride,  $\text{HgCl}_2$ .**— $0.2n$ ; dissolve 27.2 grams of the solid in water and dilute to 1 liter.

**Potassium Chromate,  $\text{K}_2\text{CrO}_4$ .**— $n$ ; dissolve 97.1 grams of the solid in water and dilute to 1 liter.



**Potassium Cyanide, KCN.**—*n*; dissolve 65.1 grams of the solid in water and dilute to 1 liter.

**Potassium Dichromate,  $K_2Cr_2O_7$ .**—*n*: dissolve 147.1 grams of the solid in water and dilute to 1 liter.

**Potassium Ferrocyanide,  $K_4[Fe(CN)_6] \cdot 3H_2O$ .**—*n*; dissolve 105.6 grams of the solid in water and dilute to 1 liter.

**Potassium Ferricyanide,  $K_3[Fe(CN)_6]$ .**—*n*; dissolve 109.7 grams of the solid in water and dilute to 1 liter.

**Potassium Iodide, KI.**—*n*; dissolve 166 grams of the solid in water and dilute to 1 liter.

**Potassium Nitrite,  $KNO_2$ .**—*6n*; dissolve 510.6 grams of the solid in water and dilute to 1 liter.

**Potassium Permanganate,  $KMnO_4$ .**—*0.2n*; dissolve 31.6 grams of the solid in water and dilute to 1 liter.

**Potassium Thiocyanate, KSCN.**—*n*; dissolve 97.2 grams of the solid in water and dilute to 1 liter.

**Silver Nitrate,  $AgNO_3$ .**—*n*; dissolve 169.9 grams of the solid in water and dilute to 1 liter.

**Silver Sulfate,  $Ag_2SO_4$ .**—Saturated solution; mechanically stir 10 grams of the solid in 1 liter of water for at least three hours. Allow to settle and decant the clear liquid for use.

**Sodium Acetate,  $NaC_2H_3O_2$ .**—*3n*; dissolve 246 grams of the solid in water and dilute to 1 liter.

**Sodium Carbonate,  $Na_2CO_3$ .**—*3n*; dissolve 159 grams of the anhydrous solid or 429.3 grams of  $Na_2CO_3 \cdot 10H_2O$  in water and dilute to 1 liter.

**Sodium Hydrogen Phosphate,  $Na_2HPO_4 \cdot 12H_2O$ .**—*n*; dissolve 119.4 grams of the solid in water and dilute to 1 liter.

**Sodium Stannite,  $Na_2SnO_2$ .**—Not kept as a stock solution but is prepared by the student just before using. See section on bismuth-ion.

**Sodium Polysulfide,  $Na_2S_x$ .**—Dissolve 480 grams of the crystallized  $Na_2S \cdot 9H_2O$  in 500 cc. water. Now add 40 grams NaOH and 18 grams S, and mechanically stir until the solids are all practically dissolved. Dilute with water to 1 liter. To prepare the monosulfide omit the NaOH and S.

**Stannous Chloride,  $SnCl_2 \cdot 2H_2O$ .**—*n*; dissolve 112.8 grams of the solid in 175 cc. 12*n* HCl and dilute with water acidified with HCl to 1 liter. Keep metallic tin in the stock bottle.

## LIQUIDS AND SPECIAL REAGENTS

**Acid Cresol Red.**—Follow instructions supplied by maker.

**Alcohol, Ethyl,  $C_2H_5OH$ .**—Concentrated solution, 95 per cent.

**Alcohol, Amyl,  $C_5H_{11}OH$ .**—Use the liquid as purchased.

**Aluminon,  $C_{19}H_{11}O_3(COONH_4)_3$ .**—Dissolve 0.1 gram of the dye in 100 cc. water and keep in dropping bottles.

**Barium Chloride—Calcium Chloride.—Precipitating Reagent.** Special reagent for the precipitation of Group II of anions. Dissolve a mixture of 61 grams solid  $BaCl_2 \cdot 2H_2O$  and 52 grams  $CaCl_2 \cdot 6H_2O$  in water and dilute to 1 liter. Let stand, and if a turbidity develops due to the presence of a sulfate impurity in the  $CaCl_2$ , filter through a double filter and use the clear filtrate.

**Bromine Water.**—Saturated solution; put 400 cc. water in a 500 cc. bottle having a ground-glass stopper. The stopper should be thinly coated with vaseline. Before transferring bromine, the hands can be rubbed with vaseline. Add 20 cc. bromine to the water in the stock bottle and always have an excess of bromine present.

**Carbon Bisulfide,  $CS_2$ .**—Use the colorless, refined product.

**Chlorine Water.**—Saturated solution; use liquid chlorine from a small steel bomb to saturate small amounts of water as needed.

**Chloroform,  $CHCl_3$ .**—Use as purchased.

**Cleaning Solution.**—Add 500 cc. technical concentrated  $H_2SO_4$  to 25 grams of solid  $Na_2Cr_2O_7$ .

**Dimethyl Glyoxime ( $CH_3CNOH$ )<sub>2</sub>.**—0.01 *n*; dissolve 6 grams of the solid in 500 cc. 95 per cent alcohol.

**Ether, Sulfuric or Diethyl,  $(C_2H_5)_2O$ .**—Use as purchased.

**Fusion Mixture.**—Mix equal weights of solid anhydrous  $Na_2CO_3$  and  $K_2CO_3$ .

**Hydrogen Peroxide,  $H_2O_2$ .**—3 per cent solution; use as purchased.

**Magnesia Mixture.**—Dissolve 100 grams  $MgCl_2 \cdot 6H_2O$  and 100 grams  $NH_4Cl$  in water, then add 50 cc. concentrated  $NH_4OH$  and dilute with water to 1 liter.

**Nitroso- $\beta$ -Naphthol,  $C_{10}H_6OHNO$ .**—Saturated solution; saturate 100 cc. of 50 per cent acetic acid with the solid.

**Potassium Acid Antimonate,  $KH_2SbO_4$ .**—0.1 *n*; add 23 grams of the solid to 950 cc. boiling water and boil for five minutes. Cool rapidly by holding the flask under tap water and add 35 cc. 6*n*

KOH. Let stand for one day, filter and dilute the clear solution to 1 liter.

**Sodium Cobaltinitrite**,  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ .—0.3*n*; dissolve 230 grams of solid  $\text{NaNO}_2$  in 500 cc. water, then add 160 cc. 6*n* HAc and 35 grams of solid  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Let stand for one day, filter and dilute to 1 liter.

**Starch Suspension**.—Prepare before using as outlined in the section on nitrite-ion.

## SOLID REAGENTS

All material is to be C. P. unless otherwise stated. The student's time should not be wasted in making "blank tests" with impure chemicals.

Aluminum, turnings or wire.

Ammonium chloride,  $\text{NH}_4\text{Cl}$ .

Ammonium nitrate,  $\text{NH}_4\text{NO}_3$ .

Borax, powdered,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

Calcium carbonate,  $\text{CaCO}_3$ .

Calcium fluoride,  $\text{CaF}_2$ .

Copper, turnings, strips or wire.

Ferrous sulfate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

Ferrous ammonium sulfate,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ .

Ferrous sulfide,  $\text{FeS}$ , technical.

Iron wire, C. P.

Lead dioxide,  $\text{PbO}_2$ .

Litmus paper, red, blue and neutral.

Manganese dioxide,  $\text{MnO}_2$ , powdered.

Microcosmic salt,  $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ .

Potassium acid sulfate,  $\text{KHSO}_4$ , fused.

Potassium chlorate,  $\text{KClO}_3$ .

Potassium chloride,  $\text{KCl}$ .

Potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ .

Potassium nitrite,  $\text{KNO}_2$ .

Potassium nitrate,  $\text{KNO}_3$ .

Sand, pulverized.

Sodium acetate,  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ .

Sodium acid phosphate,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ .

Sodium carbonate,  $\text{Na}_2\text{CO}_3$ , anhydrous.

Sodium hydroxide,  $\text{NaOH}$ .

Sodium peroxidé,  $\text{Na}_2\text{O}_2$ , powder.  
Sodium sulfite,  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ .  
Starch, any kind except "soluble."  
Tin, granulated.  
Turmeric paper.  
Zinc, granulated, As free.

LABORATORY APPARATUS AND SUPPLIES THAT SHOULD BE AVAILABLE FOR THE USE OF ALL STUDENTS

**Hydrogen Sulfide.**—A dependable supply of hydrogen sulfide must be available during all laboratory hours. For the large laboratory, the liquefied gas is the most satisfactory. By means of a pressure-reducing valve the gas can be drawn at intervals from the steel bomb and temporarily stored in a gasometer. From this apparatus it is conveyed to the hoods by means of the service lines. It is not desirable to have the steel bomb connected directly to the service line because the pressure is more difficult to regulate and in case any of the outlets are left open after laboratory hours the entire gas supply may be withdrawn. When the gasometer is in the circuit, only a part of the supply will be lost.

The second choice is, of course, the various earthenware and glass generators whose individual eccentricities must be mastered by the one in charge. (This statement is made advisedly.)

A small generator that is very satisfactory and can be made for individual use consists of a 500-cc. gas bottle fitted with a three-hole rubber stopper. Through one hole a thistle tube passes nearly to the bottom of the bottle and serves as a safety valve and pressure regulator. A glass-bend delivery tube passes through the second hole, and in the third is placed a glass rod which can be raised or lowered. The lower end of the rod is bent in the shape of a hook, and from it is suspended a perforated lead cylinder which is closed at the bottom. Ferrous sulfide is placed in the lead cylinder, and the bottle is partly filled with acid. The generation of gas can be controlled by raising or lowering the rod.

The gas supplied by any generator must be passed through a wash bottle containing water in order to remove suspended particles of ferrous sulfide.

**Hoods.**—Hoods that are placed about the walls of the laboratory are preferable to a congested arrangement in a small stench



room. The gases can be removed more readily by this arrangement, and they are far more accessible for use by the students.

**Hydrogen Sulfide Gas Outlets.**—The purpose of the outlet is to supply a slow, steady flow of the gas. Clamps attached to rubber outlet tubing frequently give trouble by leaking or, if tightened too much, may cause the inner walls of the rubber tubing to stick.

A solid glass bead, when placed in the tubing, gives satisfactory results so long as the tubing is new and elastic. The flow of gas is regulated by pinching the tubing about the bead, and when the pressure is released the tube is automatically shut.

Brass stopcocks can be placed at each outlet in the supply line and opened just enough to permit a small flow of gas. They are easily corroded, however, and with the least stoppage the tendency is to open fully. Their main purpose is thereby destroyed.

A capillary glass tube can be fitted to a one-hole rubber stopper and placed in the supply line just back of each outlet stopcock. The glass tube does not corrode and it cannot be tampered with. The outlet stopcock is turned on full when the gas is used and consequently does not become stopped up. A capillary tube in the rubber tube outlet is of very little use because it is easily broken or removed.

**Filter Pumps or Aspirators.**—If individual suction pumps are attached to the water supply outlets at the desks they should be of a type that can be taken apart readily and cleaned. Much trouble will be prevented if students will use safety bottles between the filter flask and the aspirator. If solutions and precipitates are kept out of the suction apparatus it will work satisfactorily for a long time.

A laboratory table is often equipped with a cylindrical type of aspirator which has a large capacity and is connected to a suction line that serves the entire table. For large laboratories a motor-driven suction apparatus is sometimes installed in the basement and is connected to all of the service lines.

**Steam Bath.**—A steam bath is of great assistance in evaporating solutions, particularly to dryness, because there is no danger of overheating. It can be so arranged that the steam-supply system of the building is used when the steam is turned on. The bath should be of ample capacity.

**Gas Plate.**—A rectangular iron plate in one of the hoods, heated by a special gas burner, will eliminate a promiscuous array



of individual ring stands and tripods used for acid evaporations. A special gas plate can be purchased that is heated by a series of small gas jets very similar to the ordinary kitchen gas-range oven.

**Hot-air Bath.**—A hot-air bath should be provided for drying samples and especially for dehydrating silicic acid. It can be heated by gas or electricity and is usually regulated for  $110^{\circ}$ – $120^{\circ}$ .

**Distilled Water.**—It is preferable to have the distilled water in a large supply bottle with a siphon outlet rather than a number of individual desk bottles which are kept on the desk shelves. By the latter arrangement the water soon becomes contaminated with dust and fumes in the laboratory.

**Cork Roll.**—All cork stoppers should be made pliable by means of a suitable cork roll which is screwed or bolted to a convenient table top.

**Roll of Paper.**—A 6-inch roll of thin wrapping paper with a suitable stand will enable students to tear off strips for the transfer of solids from the stock bottles to the students' test tubes. If a small square of paper is taken and folded once through the middle, the solid from a wide-mouthed bottle can be obtained without spilling. Transference can then be made to a test tube by folding the paper slightly, holding in an inclined position and tapping.

#### DESK EQUIPMENT

The non-soluble type of glassware is very essential in analytical work. It is much more durable than the common soft glass and is not attacked by ordinary reagents. Although the initial expense is slightly greater, it is more economical in the end.

Beakers, lipped type, two, 100 cc.; four, 200 cc.; two, 300 cc.

Burners, high-temperature type, Meker or Tirrill, 2. The common laboratory burner will not give satisfactory results with fusions and a blast lamp is seldom necessary when the burners just mentioned are used.

Casserole, porcelain, 100 cc.

Clamps, 2, small, for iron stand.

Cobalt glass, 3 pieces, about 2 by 3 inches.

Crucibles, porcelain, with cover, two,  $1\frac{1}{4}$ -inches diameter; one nickel, about  $1\frac{1}{4}$ -inches diameter.

Evaporating dishes, porcelain, two, 6.5 cm. in diameter; one, 10 cm. in diameter.

File,\* iron, triangular, about 6 inches in length.

Filter paper,\* 2 packages  $3\frac{1}{2}$  inches in diameter. One package to be of open texture for rapidly filtering ordinary precipitates, and one package of close texture for filtering finely divided precipitates like those in the alkaline-earth group.

Flasks, Erlenmeyer or cone type: two, 150 cc.; four, 300 cc.; one, 500 cc.

Filter flask, 500 cc.

Forceps, one pair nickel plated.

Funnels, glass, four,  $2\frac{1}{2}$  inches in diameter. One separatory funnel about 50 cc. capacity.

Funnel stem cleaner. One small-diameter bristle brush.

Gas-lighter.\* Tong-type of friction spark lighter. The use of this inexpensive device will eliminate the burned-match nuisance about the laboratory and especially in the sinks. The tips are replaceable.

Gauze,\* iron wire, 4 inches square. One piece plain, a second piece with asbestos center.

Graduate, glass graduate or graduated cylinder, one, 10 cc.; one, 100 cc.

Labels,\* 1 box small gummed labels.

Litmus paper containers, 3 small bottles or vials with tightly fitting stoppers or screw caps to hold litmus-paper strips.

Mortar and pestle, porcelain. One about  $2\frac{1}{2}$  inches in diameter.

Pipette, one, 10 cc.

Rod,\* glass, one 12 inches in length, 4 mm. in diameter.

Spatula, porcelain. Do not use the horn spatula which is decomposed by  $\text{Na}_2\text{S}_x$  and strong alkalies.

Sponge,\* about 6 inches in diameter. Keep broken glass out of the sponge; severe cuts result from wiping up broken glass on a desk top and later squeezing the sponge in the hand. Clean up broken glassware with a dust brush and dust pan.

Stands, iron, one about 20 inches high fitted with one 4-inch ring; one 3-inch ring; and two, 2-inch rings. The 2-inch rings or small clamps and the stand can be used in filtering. One filter stand of any commercial type can be provided.

Stoppers,\* 6 cork and 6 solid-rubber stoppers to fit the  $5 \times \frac{3}{4}$ -inch test tubes should be kept in the desk. Additional stoppers are obtained from the stock room as needed.

\* The articles marked \* are usually not returnable.

Test tubes: twelve,  $5 \times \frac{3}{4}$  inch; twelve,  $4 \times \frac{1}{2}$  inch. Small tubes about  $2 \times \frac{1}{4}$  inch are desirable for anion analysis. They can be supplied or made by the students from glass tubing.

Test-tube brush,\* one standard bristle brush with a bristle end.

Test-tube holder, any standard type. A holder is seldom used in qualitative analysis. Some use a folded piece of paper which serves as a strap for holding the tube when strongly heated.

Test-tube rack, 12 tube capacity.

Towels.\* Clean waste cotton or linen cloth is more serviceable than a cheap grade of toweling that is little better than a burlap. One piece of cloth should be as nearly lintless as possible for wiping glassware when necessary. The best way to dry glassware is to rinse with scalding hot water and dry in an open rack.

Triangle, one, pipe-stem type.

Tubing, glass,\* 4 mm. in diameter, 1 foot in length; rubber, two 2-foot lengths for gas burners.

Wash bottles, one, 500 cc.; one, about 250 cc.; both complete with all necessary fittings. It is desirable to wrap thin sheet cork or some other heat insulating material about the necks of the bottles.

Watch glasses, four, 7.5 cm. diameter; one, 10 cm. diameter.

The articles marked \* are usually not returnable.

TABLE XXV  
INTERNATIONAL ATOMIC WEIGHTS \*  
1928

	0-16		0-16
Actinium.....Ac	?	<b>Molybdenum</b> .....Mo	96.0
<b>Aluminum</b> .....Al	26.97	Neodymium.....Nd	144.27
<b>Antimony</b> .....Sb	121.77	Neon.....Ne	20.183
Argon.....A	39.94	<b>Nickel</b> .....Ni	58.69
<b>Arsenic</b> .....As	74.96	Niobium (Nb), see Columbium	
<b>Barium</b> .....Ba	137.37	Niton (Nt), see Radon	
Beryllium.....Be	9.02	<b>Nitrogen</b> .....N	14.008
<b>Bismuth</b> .....Bi	209.00	Osmium.....Os	190.8
<b>Boron</b> .....B	10.82	<b>Oxygen</b> .....O	16.000
<b>Bromine</b> .....Br	79.916	Palladium.....Pd	106.7
<b>Cadmium</b> .....Cd	112.41	<b>Phosphorus</b> .....P	31.027
Cæsium.....Cs	132.81	Platinum.....Pt	195.23
<b>Calcium</b> .....Ca	40.07	Polonium.....Po	(210)
<b>Carbon</b> .....C	12.000	<b>Potassium</b> .....K	39.096
Cassiopeium.....Cp	175.0	Praseodymium.....Pr	140.92
Celtium (Ct), see Hafnium		Protoactinium.....Pa	?
Cerium.....Ce	140.25	Radium.....Ra	225.95
<b>Chlorine</b> .....Cl	35.457	Radon.....Rn	222.
<b>Chromium</b> .....Cr	52.01	Ra-emanation.....Em	222.
<b>Cobalt</b> .....Co	58.94	Rhenium.....Re	
Columbium.....Cb	93.1	Rhodium.....Rh	102.91
<b>Copper</b> .....Cu	63.57	Rubidium.....Rb	85.44
Dysprosium.....Dy (Ds)	162.46	Ruthenium.....Ru	101.7
Erbium.....Er	167.7	Samarium.....Sa	150.43
Europium.....Eu	152.0	Scandium.....Sc	45.10
<b>Fluorine</b> .....F	19.00	Selenium.....Se	79.2
Gadolinium.....Gd	157.26	<b>Silicon</b> .....Si	28.06
Gallium.....Ga	69.72	<b>Silver</b> .....Ag	107.880
Germanium.....Ge	72.60	<b>Sodium</b> .....Na	22.997
Glucinium (Gl), see Beryllium		<b>Strontium</b> .....Sr	87.63
<b>Gold</b> .....Au	197.2	<b>Sulfur</b> .....S	32.064
Hafnium.....Hf	178.6	Tantalum.....Ta	181.5
Helium.....He	4.002	Tellurium.....Te	127.5
Holmium.....Ho	163.5	Terbium.....Tb	159.2
<b>Hydrogen</b> .....H	1.008	Thallium.....Tl	204.39
Indium.....In	114.8	Thorium.....Th	232.15
<b>Iodine</b> .....I(J)	126.932	Thulium.....Tm (Tu)	169.4
Iridium.....Ir	193.1	<b>Tin</b> .....Sn	118.70
<b>Iron</b> .....Fe	55.84	Titanium.....Ti	47.90
Krypton.....Kr	82.9	Tungsten.....W	184.0
Lanthanum.....La	138.90	Uranium.....U	238.17
<b>Lead</b> .....Pb	207.22	Uranium-X <sub>2</sub> .....UX <sub>2</sub> (234)	
Lithium.....Li	6.940	Vanadium.....V	50.96
Lutecium.....Lu	175.0	Xenon.....Xe	130.2
<b>Magnesium</b> .....Mg	24.32	Ytterbium.....Yb	173.6
<b>Manganese</b> .....Mn	54.93	Yttrium.....Y (Yt)	88.92
Masurium.....Ma		<b>Zinc</b> .....Zn	65.38
<b>Mercury</b> .....Hg	200.61	Zirconium.....Zr	91.22

\* The common elements are in bold-face type.





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